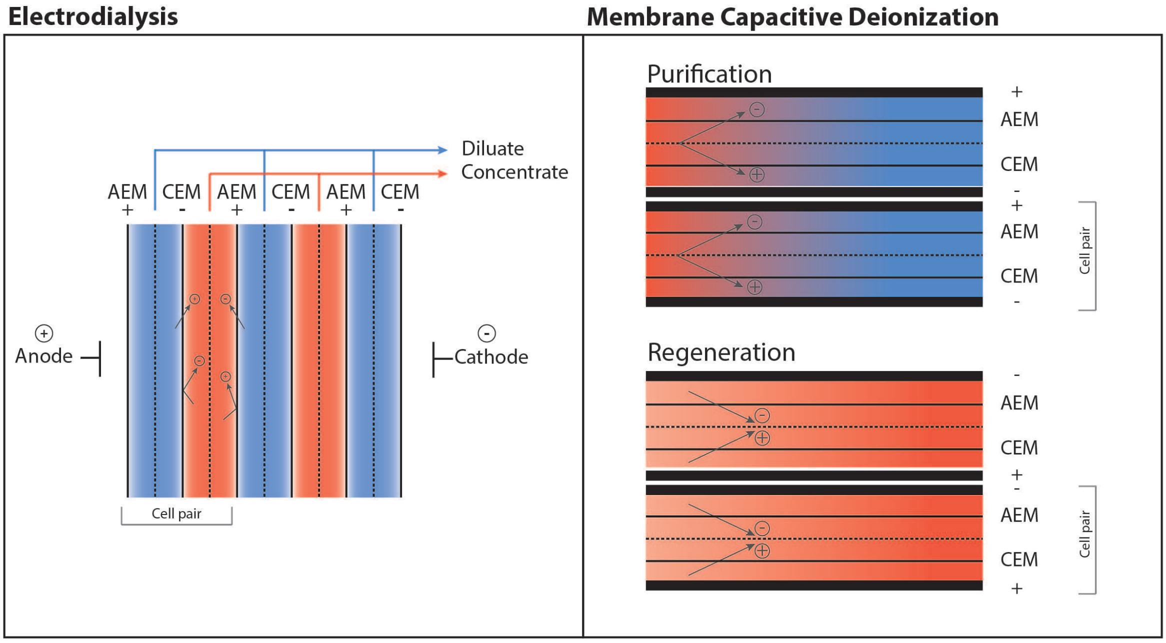
Mild desalination of cooling tower blowdown water with electrodialysis and membrane capacitive deionization: a comparative study



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June 2013

Delft University of Technology

Challenge the future

Mild desalination of cooling tower blowdown water with electrodialysis and membrane capacitive deionization: a comparative study

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I. Summary

The world is facing a water shortage and beside water reuse in the urban water cycle, is efficient water management in the industry becoming more of interest. Dow Chemical Company in Terneuzen wants to reduce its water consumption and is exploring different options for the reuse of water. One of their largest waste streams is cooling tower blowdown water (CTBD). This is a concentrated and salty (3.9mS/cm) stream which remains after the evaporative cooling process in cooling towers.

Electrodialysis (ED) and (membrane) capacitive deionization ((M)CDI) are both desalination technologies which separate dissolved ions from water based on an electrical potential difference. In electrodialysis, ions are transported through ion permeable membranes under the influence of an electrical potential gradient, creating a concentrated and a diluted water stream. In membrane capacitive deionization, ions are collected in carbon electrodes which have ion-selective membranes placed in front, over which a potential difference is created. Polarity of the system can be reversed intermittently to release the ions and restore the capacity of the electrodes.

A comparative study has been carried out between ED and MCDI for the treatment of cooling tower blowdown water. Main objective was a qualitative and objective comparison between the two technologies based on energy requirements, current efficiencies and membrane performance. The two main starting points of the experiments were: 1) desalination of similar feed water down to a conductivity of 1000µS/cm, 2) a water recovery of 66% should be achieved.

Limiting current densities (LCD) were determined for different water types in an ED batch setup. For the desalination of CTBD water, 10 successive experiments were carried out in which 1L of CTBD water was desalinated. The LCD showed to be of great influence on desalination of CTBD water with ED and was mainly determined by sodium, chloride, calcium and sulphate concentrations. The LCD increases linear with increasing salt concentration and flow rate. Main outcome of the experiments was that the ion removal remained constant while there was some, probably organic, fouling on the membranes in the first couple of experiments. Current efficiencies were observed to be 80% or higher.

Two stacks with different membrane types were tested in the MCDI experiment. With the setup, a continuous eight hour experiment was carried out with CTBD water. Due to the high salt concentrations, low flows were needed to reach the required desalination rate of the feed water by the maximum supply of 20 amperes. Due to this limitation, the water recovery was between 40% and 62% and therefore was the requirement of 66% not met. The membranes were not significantly affected by scaling and both membrane types showed similar ion removal rates. Current efficiencies were around 60% for anions and cations, which is remarkably low and probably due to the impurity of water samples.

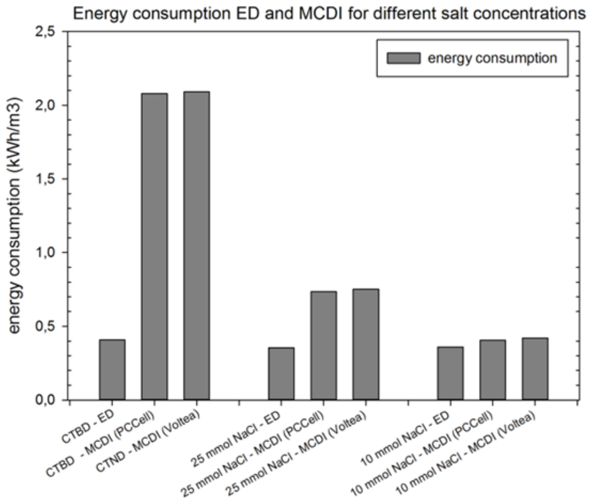

Figure 0-1 Energy requirement for 25mmol/l NaCl desalination with different current applications

Main difference between the two technologies for the treatment of CTBD water lays in the energy consumption. The results (presented in Figure 0-1) show that the energy requirement of MCDI for the treatment of CTBD water was 5 times higher than desalination with ED. Electrodialysis can desalinate CTBD water for 0.4kWh/m^3, compared to MCDI which requires 2.1kWh/m^3. When salt concentrations decrease, the energy requirement for MCDI becomes less. For the desalination of 10mmol/l NaCl the technologies become equal in energy consumption. It was concluded from these results that the treatment of CTBD water with ED was less energy consuming than with MCDI.

Based on the experimental results, a design was made for an electrodialysis pilot facility for the treatment of 4m^3/h. The pilot consists of a pre-filtration with cartridge filters and four ED stacks. Water flows successively through the stacks to obtain the required desalination rate of the water. The stacks can be operated with a different current density, which is lower than the limiting current density of the product water requirement. It is recommended to further test desalination of CTBD water with ED in a pilot study. Main advice is to run longer tests to gain more insight on the longer run performance of the membranes and the formation of biofouling.

II. Preface

This thesis is the result of 11 months research, as part of completing the Master track Watermanagement at the department of Sanitary Engineering, faculty of Civil Engineering at Delft University of Technology. The past year I have dived deep into the world of electrochemistry and made myself familiar with the interesting, but complex topic of desalination with electrochemical technologies. It was quite a challenge to understand, put up and get two setups to work. Having to work at two places and the involvement of different partners made it all together a valuable learning process of which the product now lies before you.

Although this thesis has my name on the cover, it could not have been so complete without the help of many people. Therefore I would like to take this opportunity to thank some of them;

First of all the members of my graduation committee; Luuk Rietveld, throughout my masters you have supported me in several projects and I always appreciated your ideas and supervision. You gave me the opportunity to go to South Africa to work with one of your colleagues on water treatment in rural areas. Looking back, this experience was one of the best times during my study period. For this thesis you gave me responsibilities in the E4Water project, an experience that created for me an added value to this thesis. Arne Verliefde, your knowledge on ED and (M)CDI was of great value during my thesis. You were always easy to contact by mail, Skype or in person to answer questions or explain in the theory behind certain processes. Bas Heijman, you were available for discussions or questions on my results and report. Furthermore, I would like to thank the partners of the E4Water project, and especially Wilbert van den Broek also a committee member, for all the interesting meetings and discussions we have had.

My appreciation also goes out to Bert van der Wal from Voltea for giving me the opportunity to work at Voltea with their CapDI technology. Fernando Cabedo, thank you for assisting me in my experiments. Although I did most of my experiment at Voltea, there are some people from the laboratory at TU Delft that I would like to thank. Tonny Schuit and Patrick Andeweg, with your assistance I managed to get my electrodialysis setup up and running very quickly. Sander de Vree thank you for all the supply of all electrical parts of my setup. David Moed, I appreciate your enthusiastic input in my committee meetings and your assistance with the IC measurements.

Hard work cannot be effective without time for relaxation. Therefore there are many friends whom I would like to thank, but who I cannot all mention by name. The numerous of coffees and teas, borrels, an amazing week skiing and enjoyable weekends were of great value to get my mind of this thesis. Dorine, thanks for being four doors away.

Finally I would like to thank my family; Lieve pap en mam, you have supported me throughout my studies and showed a lot of interest. You have always given me good advices and the opportunity to develop myself in different ways. Josien, your "technical sis" is finally graduated now, thanks for all the nice family time we have. Last but definitely not least, Jaco. We started our study civil engineering together, and we will graduate one week after each other. Who would have expected that? I really enjoyed our study time together, but I'm happy we each found our own field of interest. Thank you for all your support the last years, I could not have done it without it.

Marleen Heidekamp

Delft, June 2013

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VI. List of abbreviations

AEM	Anion Exchange Membrane
CapDI	Capacitive Deionization
CC	Constant Current
CD	Current Density
CEM	Cation Exchange Membrane
CTBD	Cooling Tower Blowdown
ED	Electrodialysis
EDR	Electrodialysis Reversal
E4Water	Economically and Ecologically Efficient Water Management in the European Chemical Industry
IEX	Ion Exchange
LCD	Limiting Current Density
(M)CDI	(Membrane) Capacitive Deionization
MSF	Multi Stage Flash
RO	Reverse Osmosis
NF	Nano Filtration
TDS	Total Dissolved Salts
TOC	Total Organic Carbon
WWTP	Waste Water Treatment Plant

1 Introduction

The chemical industry encompasses 5% up to 20% of the global fresh water consumption (UN, 2009) and most of this water originates from surface water. Due to the fresh water scarcity which the world will face in the near future, water reuse is becoming more and more important. The reuse of water involves two manners of saving water and safeguarding quantity and quality: 1) lessen the water intake 2) lessen the discharge of polluted water. The chemical industry provides great potential for increasing the eco-efficiency of industrial water management, because of the large consumption levels. Water reuse in the Netherlands is also a challenge in the near future since the water dependent industry is directly responsible for 20% of the total production value of the country (VEMW, 2013). This indicates that an economy without sufficient water of the right quality is inconceivable.

1.1 Project background

The European Framework Project (FP7) E4Water (Economically and Ecologically Efficient Water Management in the European Chemical Industry), addresses crucial process needs in order to overcome bottlenecks and barriers for integrated and energy-efficient water management in the (chemical) industry. The objective of the E4Water project is to develop, test and validate new integrated approaches, methodologies and process technologies so that more efficient and sustainable management of water in the chemical industry with cross-fertilization possibilities to other industrial sectors can be established (E4Water, 2012). To achieve this objective, large chemical industries, leading European water sector companies and innovative R&D centres and universities, which are active in the field of water management, are cooperating together. Within the project, six case studies are being carried out in several industries, each dealing with a sub research area of the E4Water project. The project aims to achieve an expected reduction of 20% to 40% in water use, 30% to 70% in wastewater production, 15% to 40% in energy use and up to 60% in direct economic benefits on its industrial case study sites by 2014 (E4Water, 2012).

Dow case

Dow Chemical Company is a world leading company that produces chemicals and other products. Their production site at Terneuzen, Zeeuws-Vlaanderen is the main location in the Benelux which produces millions of tons of chemicals and synthetics per year. Dow uses globally about half billion fresh water for their industry per year. The company is currently considering new industrial process installations in which brackish or light salt water can be used as an alternative for fresh water. As an example, Dow wants to focus in the coming years on the possibilities of mild desalinated water usage in cooling towers. This project is incorporated in one of the case studies of the E4Water project, in which Dow works together with several partners to investigate desalination techniques for their water streams. Aim of this case study is the mild desalination of miscellaneous water streams to achieve optimum reuse in industry or agriculture at affordable costs (E4Water, 2012). The objective of the case study is to develop a new desalination process, based on innovative concepts and existing technologies that enable the reuse of mild desalinated water in industry or agriculture. A fixed parameter for success is to produce an industrial grade water which is characterized by a conductivity of 1000µS/cm, for less than 0.40€/m³. Possible treatment technologies are investigated with laboratory tests. Based on these results, a pilot study will start in autumn 2013 studying the long-term effects of two desalination technologies with pre-treatment.

Dow has selected three potential streams, which are produced at their site, for mild desalination and reuse in the industrial water cycle. These streams are:

1. Slightly salty effluent water of the Dow waste water treatment plant (WWTP). This water has already been biologically treated and is slightly brackish (ca. 1200µS/cm). This water stream is, in general, of a constant quality throughout the year.
2. Rainwater collected in a reservoir near the premises of Dow. This water is runoff from a part of the Dow premises and a part of the surrounding natural area. The water quality and quantity of this source are affected by seasonal influences and therefore is the stream not of constant quality and quantity. The water is slightly saline (ca. 1500µS/cm) because Dow is situated in a polder next to the river Scheldt.
3. Cooling tower blowdown (CTBD) water is a concentrated stream which remains after the evaporative process in cooling towers. This stream has a fairly constant quality in time and is very saline (ca. 4000µS/cm) compared to the first two streams. The CTBD water originates from cooling towers present on the premises of Dow and from ELSTA. ELSTA is a power plant next to the site of Dow and also produces large volumes of cooling tower blowdown water.

At present, the waste water effluent and the cooling tower blowdown water are periodically discharged to the river Scheldt. The goal is to make reuse of these streams possible. Figure 1-1 gives a schematic presentation of the future water cycle around the Dow complex in Terneuzen.

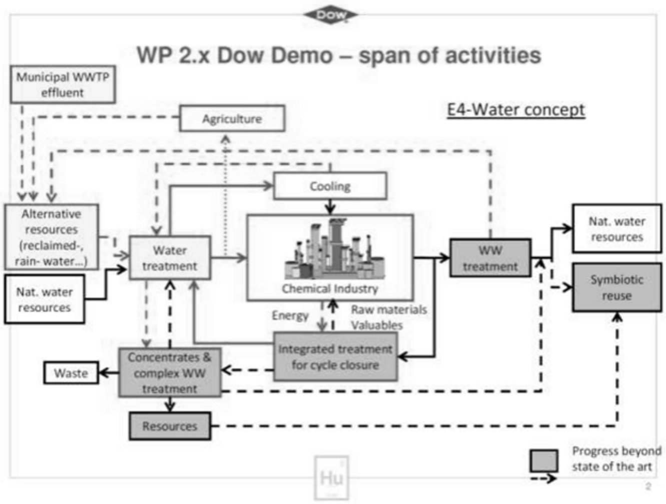


Figure 1-1 The proposed future water cycle around the Dow Chemical industrial complex in Terneuzen (E4Water)

1.2 Desalination

Desalination is the removal of dissolved salts and minerals from water. Desalination can be used for the treatment of various water resources like seawater, (industrial) waste water or for the production of drinking water. Most common desalination processes separate the saline water source into two water steams: a fresh water flow containing a low concentration of salts and a concentrated brine stream. Desalination can be achieved using different separation technologies, each requiring a specific source of energy. Worldwide, some of these technologies are common and implemented on a large scale or a pilot scale, whilst others are still in the research phase. Figure 1-2 gives an overview of desalination technologies used worldwide.

The different techniques with the potential to desalinate various water types can be categorized into different groups based on principle of operation. Based on the principle of operation, three main classifications of desalination technology exist: membrane based desalination technologies, thermal desalination technologies and electro (chemical) desalination technologies (shown in Figure 1-3) which all briefly are discussed in this paragraph.

A more detailed overview of the different desalination technologies is presented in factsheets in Appendix A. In the factsheets the technologies are described by their operational principle, obtained water quality and typical operational parameters. Also an indication of operational and capital costs is given.

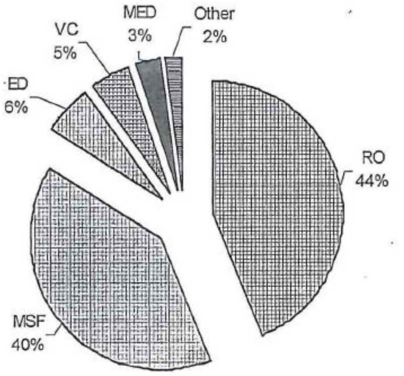


Figure 1-2 Desalination processes most commonly used worldwide (IDA, 2002)

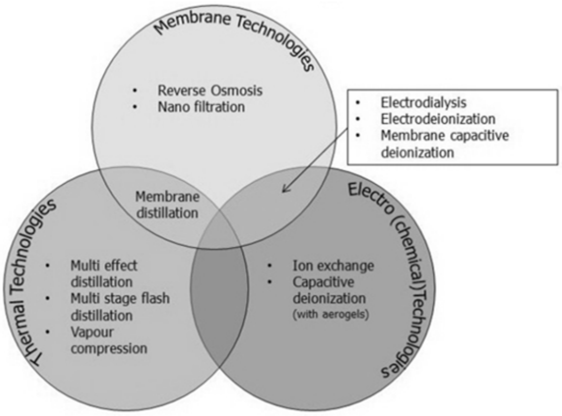


Figure 1-3 Classification of desalination technologies

1.2.1 Membrane technologies

Membrane filtration is a physical separation technology, mainly based on size exclusion. Water is pressurized and pushed through a membrane with a certain pore size. Water and particles smaller than the pore size can flow through the membrane, while particles larger than the pore size are retained on the membrane. Reverse Osmosis (RO) and Nano Filtration (NF) are the most commonly known membrane techniques and can treat water with high salinities. Main difference between RO and NF is the pore size of the membrane, which is smaller for RO applications. The smaller pore sizes involve a higher pressure requirement to filter the water through the membranes. Up to 99% of the mono and divalent ions can be retained in RO. Divalent ions can be retained up to 99% in NF (Nalco, 2009). To a large extend other constituents in the water, like particles and viruses, are removed with both RO and NF. Therefore these membrane technologies produce high quality, desalinated and disinfected water. Water recovery of RO and NF systems can be up to 90% (AWWA, 2004). Main operational problems with RO/NF installations are biofouling and scaling on the membranes. Therefore adequate pre-treatment is required to remove organic, colloidal and biological matter in order to ensure a stable influent water quality for the RO/NF installation and to achieve an economically viable process. Both NF and RO are mature technologies that are applied all around the world for the desalination of large volumes of different water types (Fritzmann, 2006).

1.2.2 Thermal technologies

Thermal desalination is a distillation processes in which energy is used to heat water. This heated water is successively introduced into several vessels where the pressure is lowered after each stage. Due to the stepwise lowering of the pressure, water continues to boil and will evaporate. The evaporated water is condensed to collect purified water at each stage. Multi stage flash (MSF) evaporation is an example of a thermal technology which operates in the above described way. Main operational problems with MSF are scaling of the heat transfer surfaces, which reduce the effectiveness of the system drastically (AWWA, 2004). Proper pre-treatment such as the removal of particles by filtration, is required to enhance the efficiency of the operation of the system. Thermal techniques are generally used for the desalination of large volumes of seawater and in areas where waste heat is available or where energy is cheap.

Membrane distillation is a technology which combines an evaporative process with membrane separation. Saline feed water is heated to a certain temperature and introduced into the installation. Due to the elevated temperature water evaporates and passes through the dry hydrophobic membranes. A lower temperature is present on the other side (the permeate side) of the membrane, causing the water vapour to condense, after which pure water (Total Dissolved Salts (TDS) <10mg/l) is collected. Main point of particular interest is the heat supply for this system and it can for example be beneficial to make use of residual heat (Jansen et al.).

1.2.3 Electro (chemical) technologies

Electro (chemical) processes is a collective term for all technologies which remove charged ions from water by a chemical process, or with the use of a direct current. The process of ion-exchange (IEX) is based on the removal of specific ions or compounds from a stream by the exchange of a pre-saturated ion with the target ions on cation and anion exchange resins. Once the resins are saturated, they can be regenerated using chemicals. The frequency of regeneration is determined by the feed water quality. If the resins need to be regenerated very often, the technology might become less interesting for economic reasons. IEX is a commonly applied process in drinking water treatment for the removal of hardness and in industrial water for the production of deionized water. IEX can also be used as a desalination process for mild brackish and brackish waters and is robust for influent water qualities (Prajapati, 1985). With ion exchange low effluent possibilities, up to <1.0mg TDS/l, can be achieved after proper pre-treatment for mainly the removal of particles.

Electrodialysis (ED) and (membrane) capacitive deionization ((M)CDI) are examples of desalination technologies which separate dissolved ions from water based on an electrical potential difference. In ED, ions are transported through ion permeable membranes under the influence of an electrical potential gradient. The ion exchange membranes selectively pass cations (cation exchange membranes) or anions (anion exchange membranes) ions, and reject the oppositely charged ions. This way, a concentrated stream and a stream which depletes of ions is created. In CDI, ions are collected in carbon electrodes over which a potential difference is created. In MCDI, ion selective membranes are placed in front of the electrodes to improve the efficiency. Polarity of the system can be reversed intermittently to release the ions and restore the capacity of the electrodes.

1.3 Research framework

Cooling tower blowdown water is an industrial stream that is challenging to treat due to high salt concentrations and presence of other additives. The composition and the large volume of this stream at the Dow site, makes it a challenging water stream to treat, which is presumably not economically interesting for all desalination technologies. Electrodialysis and membrane capacitive deionisation are in particular interesting for the application of industrial waters since these techniques primarily remove salts. The technologies have great similarity in working principle but there are also differences. Electrodialysis has proven its maturity with large scale applications all around the world (Strathmann, 2010), whereas membrane capacitive deionization is a new and innovative technology which is still being researched and is not yet applied on a large scale. However, it is stated that MCDI is a process that holds promise for not only being a commercially viable alternative for treating water but also an energy saving alternative (Anderson, 2010).

Up to now, limited experiments have been carried out to quantitatively compare these two technologies. By comparing them under similar conditions, such as equal salt removal and water recovery with the same feed water, insights in their performance based on energy consumption, ion removal and scaling can be gained. Besides are ED and MCDI technologies that can compete with reverse osmosis (RO). RO is a technology which has proved its maturity and is used for the desalination of sea and brackish water on large scale (Fritzmann, 2007). By comparing the performance of ED and MCDI to that of RO, on objective criteria, the maturity and potential of ED and MCDI technologies can be assessed.

The consideration and the framework given above leads to the following research question of this thesis:

1.3.1 Main research question

"Are electrodialysis and membrane capacitive deionization suitable technologies for the desalination of cooling tower blowdown water, down to a conductivity of 1000µS/cm, and what are the main differences in operational parameters between the two technologies?"

Sub questions are formulated to discuss specific aspects of the main question. Afterwards, answers to these sub questions will be clustered to formulate and answer to the main research question.

1.3.2 Sub questions

- What is the water quality achieved with electrodialysis and membrane capacitive deionization when treating cooling tower blown?
- What are the optimal operational parameters for both desalination techniques?
- Is there a difference in current efficiency of different ions for both technologies?
- What is the energy consumption of both systems and how is it influenced by lay-out of the system and the salt concentration of the water?
- How does the overall performance of ED and MCDI found in the experimental results relate to the treatment of cooling tower blowdown water with reverse osmosis?
- How can the experimental results be translated into a pilot configuration?

1.4 Thesis outline

This thesis is divided in seven different chapters. In Chapter 1 the project background and research questions have been outlined.

Two desalination technologies have been extensively studied in the project, and are presented separately in the first part of this thesis. In Chapter 2 a theoretical background is given of both ED and (M)CDI. Chapter 3 presents the materials and methods for the experiments to treat the cooling tower blowdown water with the two different technologies. Chapter 3 also presents an outline of the procedure to compare the two technologies on objective criteria. The results and discussion of the experimental work with ED and MCDI is presented in Chapter 4.

In Chapter 5, electrodialysis and membranes capacitive deionization are quantitatively and objectively compared based on the results of the experiments. It is discussed how the technologies compete and at which point they are different from each other.

Chapter 6 discusses how electrodialysis can be scaled-up for a pilot application. System configuration, operation and costs are parameters which are taken into account for an electrodialysis pilot design with a capacity of 4m^3/h.

Finally, in Chapter 7 conclusions of this research and recommendations for further research are given.

2 Theoretical background

Understanding of the processes of desalination is crucial in the process of designing and elaborating experimental results. In this chapter, first an introduction on cooling tower blowdown water and its quality is explained. Next, the theory of electrodialysis and membrane capacitive deionization is discussed. Finally, characteristics of ion selective membranes are outlined because they are a key factor for both technologies.

2.1 Cooling tower blowdown water

Cooling towers provide an important process on a lot of industrial sites. They cool warm water which is produced in the industry, by an evaporative process. There are different configurations of cooling tower systems. An example of a system is given in a flow diagram in Figure 2-1. Cool water is taken in and treated to certain feed water which is used in an industrial process (e.g. electricity plant). The cool water is used in for example a heat exchanger, where after the water leaves the process with an elevated temperature. This warm water needs to be cooled down and often treated before it can be discharged or reused. Cooling of the water stream takes place in a cooling tower. The warm process water is introduced in a cooling tower where cool and dry air is blown in from the bottom, into the tower. In the tower, part of the warm water evaporates and water vapour escapes at the top of the tower into the air. Not all water condenses; a waste stream is left after the cooling process. This water is called cooling tower blowdown, which is a concentrated stream rich of salts, minerals and other components. The percentage of water left after the cooling tower in relation to the original volume of the water stream is called the thickening factor. The cooling towers of Dow function at a thickening factor of 4-5.

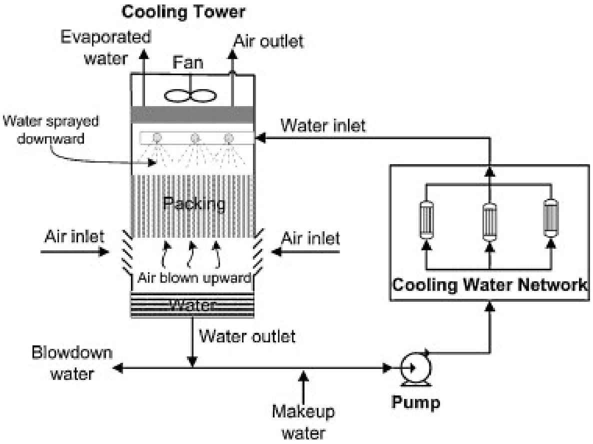


Figure 2-1 The cooling tower process (Ponce-Ortega, 2010)

The cooling tower blowdown water which is supposed to be reused in the future is produced by several processes on the Dow site. Besides the blowdown produced on the Dow site, there is CTBD water available from ELSTA, which is an energy plant located next to the site of Dow in Terneuzen.

The blowdown is a water source that is continuously available and of fairly constant quality, with an average conductivity of 4000µS/cm. Sodium, chloride, calcium and sulphate are the salts which attribute to most of salt concentration of the water. Additives like corrosion inhibitors, antiscalants and copper inhibitor (sodium benzotriazole) are often used in process water and appear in high concentration in the blowdown water. Also pH adjustment influences the water quality due to the dosing of H_2SO_4. Presence and concentration of these compounds, and the high salt concentrations can be of great influence of the treatment possibilities of this water. The estimated volume of the total cooling tower blowdown water is 1.000.000m^3 per year. At present, all cooling tower blowdown from the site of Dow is discharged two times a day into the river Scheldt, without any treatment. Aim is to produce an industrial grade water with conductivity of <1000µS/cm. The other product water requirements and the average water quality of the ELSTA CTBD water are given in Table 2-1.

Table 2-1 Cooling tower blowdown water quality and product water quality requirement

Ion/compound	**Average concentration cooling tower blowdown**	**Product water quality needs**
Conductivity, µS/cm	3500-4500	<1000
TSS, mg/l	< 5	0-1
TOC, mg/l	73.2	5-15
pH	7-8	6.5-8.5
Temperature, °C	25-30	<20
Chloride (Cl^-), mg/l	513.8	90-150
Phosphate (PO_4^{3-}-otho), mg/l	3.2	0-1
Bicarbonate (HCO_3^-), mg/l	51.0	-
Nitrate (NO_3^-), mg/l	135.4	10-20
Sodium (Na^+), mg/l	282.9	-
Potassium (K^+), mg/l	97.4	-
Calcium (Ca^{2+}), mg/l	493.8	-
Magnesium (Mg^{2+}), mg/l	64.2	-
Sulphate (SO_4^{2-}), mg/l	1280.5	-
Silicate(SiO_2), mg/l	0.92	-
Barium (Ba^+), mg/l	0.15	-
Strontium (Sr^+), mg/l	1.2	-
Iron (dissolved), mg/l	1 - 1.5	<0.2

2.2 Electrodialysis

2.2.1 Principle

Electrodialysis (ED) is a potential-driven separation process. Dissolved ions are separated from water through ion permeable membranes under the influence of an electrical potential gradient. Ion exchange membranes selectively transport positive (cation exchange membranes, CEM) or negative (anion exchange membranes, AEM) ions, and reject ions of the opposite charge. These membranes are arranged in an alternating way between the anode and cathode and an aqueous stream is introduced in between all membranes. With this configuration, positively charged cations migrate towards the cathode; they pass through the cation-exchange membrane and are rejected by the anion-exchange membrane. The opposite process occurs for anions in the feed water and the process is illustrated in Figures 2-1 and 2-2. One cell pair is defined as an anion elective membrane, a diluate compartment, a cation selective membrane and a concentrate compartment. This is the repeating unit in a stack. The mass transport of the ions in the water and membranes can be described by diffusion, convection and migration as given in the Nernst-Planck equation (Schlögl, 1964). The above described process results in an alternating ion concentration increase in one compartment (concentrate), and ion depletion in the other compartment (diluate). The cathode, as well as the anode side is bounded by a CEM to prevent chlorine ions to leak into the electrode rinse cell resulting in the formation of chlorine gas at the anode which would damage the membranes. The electrode rinse solution generally contains anions such as SO_4^{2-} which has a standard potential less negative than that of oxygen.

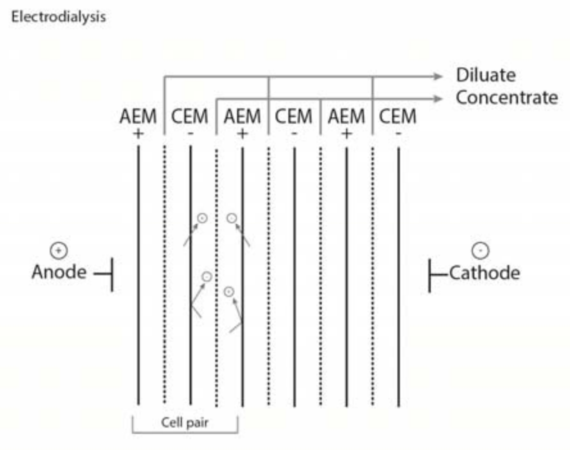


Figure 2-1 Ion removal principle in electrodialysis

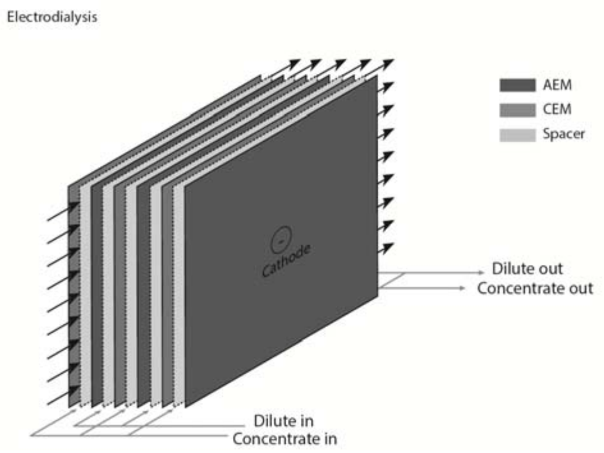


Figure 2-2 Flow scheme in electrodialysis

Electrodialysis is generally operated at constant current (galvanostatic), so that there is an equal amount of charge introduced in the system over time. When this current is established between the electrodes, electrode reactions will occur at the cathode and anode. Thereby realizing the transformation from ionic conduction to electron conduction, and thus providing the driving force for ion migration. By the use of inert metal electrodes, the transition is accomplished by the addition or subtraction of electrons to or from the ions present in the solution. Positively charged cations are reduced at the negatively charged cathode by receiving electrons; the so-called reduction reaction. Negatively charged anions are oxidized at the positively charged anode by the discharge of electrons: the oxidation reaction.

The electrode reaction is the decomposition of water and the production of oxygen, hydrogen and electrons according to the following reactions:

- Reduction reaction at the cathode $2H^+ + 2e^- \rightarrow H_2$
- Oxidation reactions at the anode $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

2.2.2 Development and applications

Electrodialysis (ED) is a technique used for over more than 50 years in the production of water from brackish sources (Strathmann, 2010). The technology became commercially available in the fifties after the first ion selective membranes were developed in the forties. One of the first commercial applications was supplied to an oil industry in Saudi Arabia (Reahl, 2006). A step towards the increase in large-scale application of ED was the introduction of electrodialysis reversal (EDR) in 1974 (Katz, 1979). With EDR the direction of ion flow is changed by reversing the polarity. Salts and other components are released from the ion exchange membranes using this system. It provides a method of cleaning and can almost eliminate the need for periodic antiscalant dosing or acidic and caustic cleaning of the membranes.

ED(R) currently has applications in the desalination of brackish water, treatment of water streams in the food and chemical industry and the production of table salt. One of the largest EDR applications was opened in 1995 in Florida where 45.000m^3/day of drinking water is produced from groundwater with a calcium sulphate concentration of 1.300ppm (Reahl, 2006)

2.2.3 Design and operation

There are two stack designs commonly applied in large scale applications of ED: sheet and tortuous. In a tortuous path flow stack, the compartments are horizontally arranged in which a long and narrow flow path is lined. This configuration allows for a high feed flow velocity (6-12cm/s) which has a positive effect on the control of concentration polarization. In a sheet flow stack, the compartments are vertically arranged and only a short process path is present. Feed flow velocities are generally quite low (2-4cm/s), which results in lower mass transfer efficiency, but also lower pressure drops compared to a tortuous configuration (Strathmann, 2010)

Electrodialysis can be operated in a continuous mode or in a feed and bleed system. In this last configuration, part of the concentrate is recirculated during the process. To realize the required salt removal and a high water recovery, staging is required. With staging, ions are removed from the feed water in several ED(R) stacks. In each successive stack is the ion concentration lowered. Staging has an advantage in energy consumption because the constant current applied on each stack, can be decreased in each stage. Therefore can each stage be operated below the limiting current density of the water quality in that stack.

2.2.4 Diluate quality

In ED(R) the degree of desalination that can be achieved in passing a feed solution through a stack is a function of the solution concentration, the applied current density and the residence time of the solution in the stack. Also the membranes influence the ion removal and ion selectivity. Salinity concentration in the diluate is strongly determined by the electric potential. It should be taken into account that neutral particles are not removed. This for example involves that the diluate is not disinfected and can still contain small neutral particles such as organic material and bacteria. These substances can for example be removed in the pre-treatment of the feed water or post-treatment of the diluate. Pre-treatment mainly requires the removal of particles as ED is a robust process which can deal with varying influent water qualities.

2.2.5 Limiting factors in efficiency

There are two important factors influencing the efficiency in practical applications of electrodialysis: current efficiencies and the limiting current density.

Current efficiency

The applied electric current can be related to the migration of ions through the ion exchange membranes. The current utilisation is 100% under ideal circumstances which means that all of the supplied charged (electrons) is used for the migration of ions. Deviation of this ideal behaviour is denoted with the current efficiency. The current efficiency relates the supplied charge to the transport of ions through the ion exchange membrane as shown in the following Equation 1.

$$CE_{\,ED}(\%) = \frac{z * F * Q_f * \sum anions/cations\,(C_{feed} - C_{diluate})}{N * I} * 100 \tag{1}$$

In which:
z is charge of the ion
F is Faraday's constant = 96485 mol/A.s
Q_f *is the flow rate of the diluate/pure water in L/s*
C_{feed} *is the concentration of an ion in mol/L*
$C_{diluate}$ *is the concentration of an ion in mol/L*
N is the number of cell pairs
I is the applied current in A

The efficiency is influenced by several factors which can contribute to incomplete current utilization (Strathmann, 2004). These effects are influenced by the system design and operating parameters and can be limited by a good design.

- Incomplete membrane selectivity;
- Non-perpendicular current transport across the ED(R) stack;
- Water transport across the membranes from the diluate to the concentrate solution due to osmotic effects;
- High current densities and low salt concentration, which result in water splitting.

Limiting current density

In the diluate cell, the salt concentration at the membrane surface is decreased and in the concentrate cell this concentration is increased. Concentration polarization is a phenomenon which has consequences in electrodialysis which are ambiguous. In electrodialysis is concentration polarization the result of differences in the transport numbers of ions in the solution and in the membrane. Figure 2-4 illustrates the effect of concentration polarization. In this figure the salt concentration profiles and the fluxes of cation and anions in the concentrate and diluate solution at the surface of a cation exchange membrane are shown. Symbols J and C denote the fluxes and the concentrations of ions. The subscripts c and a, refer to anion and cation. Superscripts mig and diff refer to migration and diffusion, superscripts d and c refer to diluate and concentrate solution and the superscripts b and m to bulk phase and membrane surface.

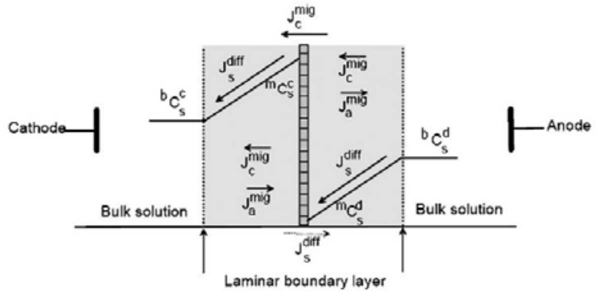


Figure 2-4 Concentration profiles of a cation exchange membrane

When, due to concentration polarization, the salt concentration at the membrane surface in the concentrate cell exceeds the limit of solubility, precipitation of salt may occur. This results in an increase in electrical resistance and possibly in membrane damage. If, due to concentration polarization, the salt concentration at the membrane surface in the diluate cell is reduced to zero, no more ions are available to transport the electric current. This results is the establishment of an increase in voltage drop across the boundary layer due to water splitting and an increased resistivity due to the locally, very low salt concentrations. Water splitting will occur and resulting in a loss of current utilization together with a pH shift. In case of water dissociation the pH will increase at the surface of the anion-exchange membrane in the concentrate containing cell and a decrease of the pH value at the surface of the cation exchange membrane in the concentrate. The change of pH near the membranes is not desirable, because low pH values can damage the membranes and high pH values can lead to the precipitation of multivalent ions on the membrane surface (Strathmann, 2004).

Hence, the limiting current density (LCD) is defined as the maximal current density that can be transported by ions present in a certain water type over a certain membrane area, without water splitting occurring. The limiting current is different for all salts, concentrations and depends on the velocity of the feed water in the system. The limiting current density increases with increasing salt concentration and linear velocity (Lee et al. 2006).

Limiting current density can be determined theoretically (Strathmann, 2004). Since some factors in this theoretical determination of the LCD are difficult to determine, Lee et. al (2002) derived a widely accepted empirical method to determine the limiting current density as a function of the feed flow velocity for a single cell pair. Figure 2-5 shows an example of such a plot in which the bend in the graph presents the LCD. Cowan and Brown (1959) derived an empirical method for the determination of the limiting current density over a multi cell stack. In this method the overall resistance, corrected for the electrode reactions, is plotted versus the reciprocal of the current density. The minimum in this graph is the LCD of that water; an example is given in Figure 2-6.

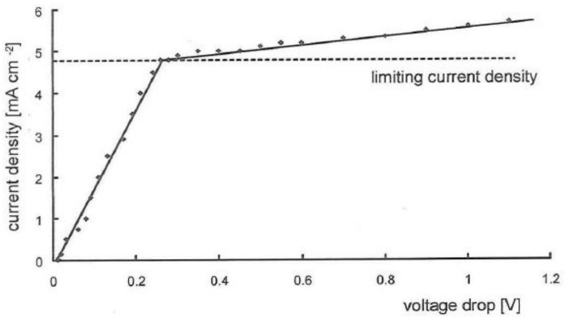


Figure 2-5 Experimental determination of the limiting current density with a single cell

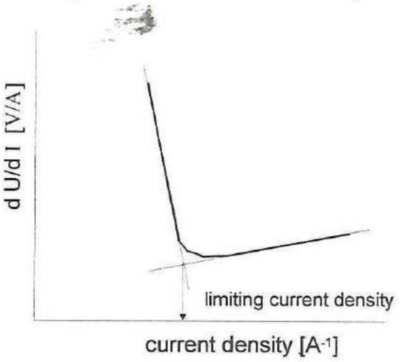


Figure 2-6 Experimental determination of the limiting current density with multiple cells

2.3 Membrane capacitive deionization

2.3.1 Principle

Capacitive deionization (CDI) is a technology which works by passing water between two oppositely charged electrodes, separated by an inert spacer to provide a channel for water to flow and to prevent the electrodes touching resulting in a short circuit. It is operated in a cycle of two processes; purification and wasting. During the purification phase a low voltage, typically 1.2V, electric field is applied to electrosorb ions in the electrical double layers in the micropores of the porous carbon electrodes that are used (Biesheuvel, 2011). During the waste phase the current is stopped or reversed, and the electrosorbed ions are released into the bulk solution, producing a concentrated brine stream. Although classical capacitive deionisation is effective for the treatment of brackish water, the addition of ion exchange membranes across the electrodes allows for a great performance increase in terms of the current efficiency and the selective uptake and release of ions (Zhao, 2012). In membrane capacitive deionisation, cation selective membranes are placed in front of the negatively charged electrode and anion selective membranes are placed facing the positively charged electrode, which together form one cell pair. In this way counter ions can freely move into and out of the electrode, while co-ion transport is blocked. The addition of an ion exchange membrane prevents thus release of co-ions from the electrode allowing much higher current efficiencies to up to 97% for membrane capacitive deionisation (MCDI) as compared to around 60% for capacitive deionisation (Biesheuvel, 2010). The application of ion selective membranes also allows for the possibility to reverse the polarity of the electrodes, which enhances the ion release from the electrodes. This is not possible in CDI because co-ions will in that case be adsorbed on the opposite electrode during the ion-release step, which does not result in an effective decrease in salt concentration (Biesheuvel, 2010). Mass transport in membrane capacitive deionization is a combination of complex mechanisms. Biesheuvel and van der Wal (2010), proposed a detailed process model for transport and mixing behaviour in the spacer compartment. The process of membrane capacitive deionization is presented in Figures 2-7, 2-8 and 2-9.

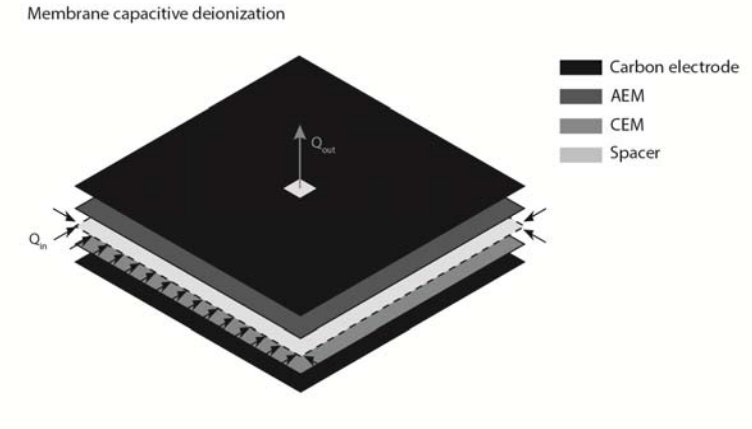


Figure 2-7 Flow scheme in membrane capacitive deionization

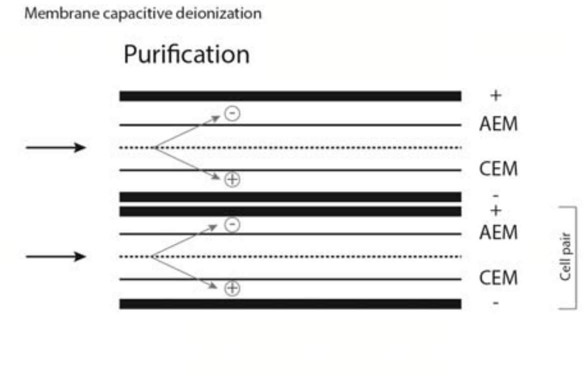


Figure 2-8 Ion removal in membrane capacitive deionization

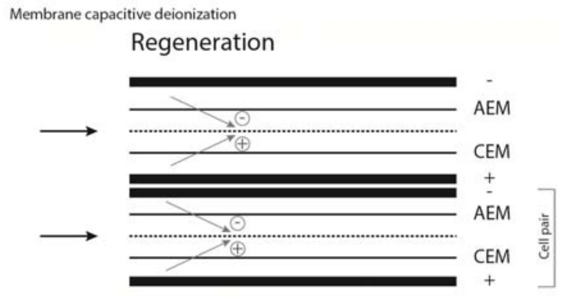


Figure 2-9 Ion release in membrane capacitive deionization

2.3.2 Development and applications

Capacitive deionisation is a desalination technique which has been studied since 1970 (Oren, 2008). However, (M)CDI up to now, has not yet been applied on large scale, and is still being researched in pilot studies and laboratory testing. The main application in these studies was the treatment of light brackish water and cooling tower makeup water. The main focus in these studies was laid on the research of organic fouling, scaling and operating modes of the system (Oren, 2008). As limited experience on long term testing is available in literature, little is still known about the membrane lifetime, operation stability and operational problems in MCDI. The main advantage of the process is the relatively low energy requirement due to the low applied electric field (1.2V) and high current densities. A drawback of this is the relatively large surface area of electrodes needed for desalination of highly concentrated waters (Strathmann, 2010)

There are several start-up companies who are developing MCDI and commercializing it. Atlantis is an American company which uses the principle of MCDI for their radial deionisation. Voltea is a Dutch start-up company which develops its CapDI for a number of applications and different scales for several industries.

2.3.3 Design and operation

A MCDI stack consists of multiple cells. One cell is build up from a spacer sandwiched by cation and anion selective membranes which are both covering a carbon electrode. The total thickness of one cell is in the order of 1 millimetre (Biesheuvel, 2011). A commercial unit can hold multiple stacks, which enlarges the desalination capacity of a unit. Water is introduced on the outside of the stack from where it flows in between the electrodes and membranes towards the middle of the stack where the desalinated water is collected.

MCDI is operated with a constant current which allows a stable permeate quality (Zhao, 2012). The salt removal percentage is set by the combination of three main operational parameters: the flow during purification and waste, the current during purification and waste, and the time interval of the two phases. With a lower flow, ions have more time to be transported towards the electrodes. By applying a higher current more ions are transported towards the electrodes. The process of MCDI is thus tuneable, which means that the salt removal can be set to a certain value.

The combination of flow rate and time interval of the phases determines the water recovery, which is expressed by the following equation:

$$Water\ recovery\ MCDI = \frac{V_{pure}}{V_{feed}} * 100\% \tag{2}$$

$in\ which{:}\ V_{feed} = V_{pure} + V_{pre-pure} + V_{waste}$

2.3.4 Water quality

MCDI produces two streams during regular operation: a waste stream and a purified stream. In a multiple stack design, the separation of these flows is regulated by an automatic valve. The waste stream is highly concentrated because it contains all the salts released from the electrodes during the wasting. The purified water is depleted of salts and can have conductivity lower than 100µS/cm depending of the feed water quality. As MCDI removes only charged ions, permeate water is not disinfected and can for example contain small neutral particles and organic material.

2.3.5 Limiting factors

There are two factors which are of influence on the efficiency in practical applications of membrane capacitive deionization: electrode capacity and current efficiencies.

Electrode capacity

The carbon electrodes are a key component in the MCDI process because the number of ions absorbed is directly proportional to the surface area of these electrodes. This has led to extensive research on the carbon electrodes in the past years (Porada, 2013). Activated carbon and carbon nano-tubes are promising materials for the preparation of carbon electrodes since their specific surface area can be up to 1100m^2/g (Strathmann, 2010). According to Oren (2008), the following properties are of importance for a good performance of electrodes in (M)CDI:

- A large specific surface area for electro sorption;
- A high electronic conductivity;
- A fast response of the entire surface area to electro sorption and electro desorption changes;
- Chemical and electrochemical stability over a wide pH range and the presence of oxidants, and the ability to tolerate voltage changes;
- Easily shaped according to the design requirements;
- A low tendency for scaling, biofouling and organic fouling.

Current efficiencies

The electric current impressed at the electrodes is not necessarily the same current that passes through the cells or deionizing compartments. The current efficiency is the fraction of input number of equivalents that is actually used for ion removal by input of electricity. It is important that the electrodes are very close to each other, separated by a thin spacer and the ion-selective membranes, in order to enhance the efficiency of the system. Current efficiencies are for example negatively affected by bypasses along the electrodes. These bypasses can be established if the membranes, spacers and electrodes are not compressed well in the production of the stack. With MCDI water splitting is generally not an issue due to the small flow channel and the high velocities which are used to flow the water through the stack.

Current efficiencies can be calculated based on conductivity and ion concentration according Equation 3. In perfect current utilization, the sum of the current efficiency of all anions and cations is both 100%.

$$CE_{MCDI}\ (\%) = \frac{z * F * Q_f * \sum anions/cations\ (C_{feed} - C_{diluate})}{I} * 100 \qquad (3)$$

In which:
z is the valance of the ion
F is Faraday's constant = 96485 mol/A.s
Q_f is the flow rate of the diluate/pure water in L/s
C_{feed} is the concentration of an ion in mol/L
$C_{diluate}$ is the concentration of an ion in mol/L
I is the applied current in A

2.4 Ion selective membranes

Ion selective membranes are a key component in both electrodialysis and membrane capacitive desalination. Their properties are of great influence on the technical feasibility and economics of the desalination process. In this paragraph the principle, characteristics and operational aspects of ion selective membranes are explained.

2.4.1 Principle

Ion selective membranes are composed of swollen gel-type polymer structures which carry fixed positive or negative charges. They can be compared with an ion-exchange resin in sheet form. Anion and cation exchange membranes are the two membrane types which are both used in ED and MCDI. The anion-exchange membranes have positively charged groups attached to the polymer matrix (i.e. $-NH_2R$). In cation-exchange membranes, these functional groups are negatively charged (i.e. $-SO_3^-$).

Figure 2-10 presents a schematisation of the matrix of a cation-exchange membrane with fixed anions and mobile cations. In this membrane structure, the fixed anions are in an electrical equilibrium with mobile cations in the interspaces of the polymer. The mobile cations are the ions present in the feed solution and are also referred to as counter-ions. These ions are thus of opposite charge with respect to the fixed ions on the polymer matrix. The mobile anions in a feed solution are the co-ions of a cation-exchange membrane, and are more or less excluded from the membrane matrix because of their electrical charge which is identical to that of the fixed ions. This is called Donnan exclusion. Due to the Donnan exclusion of the co-ions, cation exchange membranes are preferentially permeable for cations. The above described principle works exactly the same for anion exchange membranes. Only now the cations are fixed on the polymeric membrane structure, and the anions are the counter ions. Therefore the anion exchange membranes are preferentially permeable for anions.

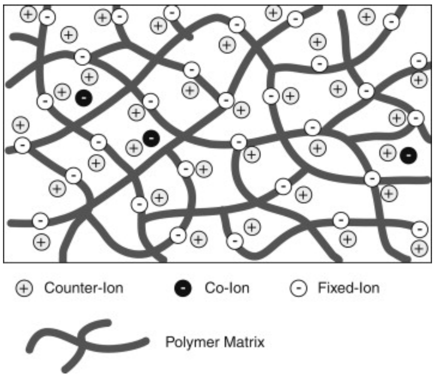


Figure 2-10 Structure of a cation selective membrane (Strathmann, 2004)

2.4.2 Membrane characteristics

Ion exchange membrane properties are determined by the base polymer used for the fabrication of the membrane. The properties determine the mechanical, chemical and thermal stability of the membrane. Ion selective membranes can be divided into two groups, according to the way the charged groups are connected to the base polymer. In homogeneous membranes, the charged groups are chemically bonded to the membrane matrix. In heterogeneous membranes, the charged groups are physically mixed with the membrane matrix (Xu, 2005). The type and concentration of the fixed charges determine the permselectivity and the electrical resistance. Membrane permselectivity is determined by the ion concentration in the membrane and especially by that of the co-ion, which is the ion carrying the same charge as the fixed ion on the membrane matrix. A completely permselective membrane should completely exclude co-ions from the membrane phase. The most desired properties of an ion selective membrane are according to Strathmann (2010):

- A high permselectivity - the membrane should be permeable for counter-ions only, but impermeable for co-ions;
- A low electrical resistance – the permeability of an ion exchange membrane should be as high as possible for the counter ions, under the driving force of an electrical potential gradient;
- Good mechanical form and stability - the membrane should be mechanically strong and stable for changes in ions solutions;
- High chemical and thermal stability - the membrane should not be affected or damaged by changes in pH and the presence of oxidising agents and organic solvents.

The combination of the characteristics and the nature of the membrane also determine the ion preference of the ion selective membrane. There are for example membranes available which reject divalent ions salts such as calcium sulphate and magnesium sulphate, but pass monovalent ion salts like NaCl (Saracco, 1994).

Depending on the feed water quality and the desalination rate, membranes can be selected for different applications.

2.4.3 Membrane fouling and cleaning

Membrane processes are affected by the presence of organics, high salt concentrations and other substances like colloidal particles. These feed water constituents can cause scaling and fouling on the membrane surface. Scaling is the precipitation of salts such as $CaSO_4$ and $CaCO_3$ when their solubility limit is surpassed, which mainly occurs on the concentrate side of an ion selective membrane process. A major problem which affects the efficiency of almost all membrane separation processes is membrane fouling. This fouling on the membranes is caused by for example the precipitation of colloids, humic acids, surfactants and biological material. The formation of a layer of biological material on the membrane is called biofouling. The formation of this layer is a slow process and can occur only after a long operation period. As colloids and other organic material are negatively charged, anion selective membranes will be affected by fouling due to the presence of the compounds in natural waters (Korngold, 1970). Fouling and scaling on membrane surfaces increases the resistance of the system, this results in a higher energy demand for desalination.

Scaling in membrane processes can be limited by a good stack design. Flows should be high enough to limit concentration polarization effects in the boundary layers. An acid wash of the membranes can be applied in case scaling does occur on the membranes. Biofouling can be removed from anion exchange membranes by an alkaline cleaning. Capacity of the membranes which have been fouled with organic material can be restored almost completely, as shown in previous experiment by Korngold et. al (1970). In case of membrane cleaning for both scaling and fouling, acid cleaning should be carried out before alkaline cleaning. Both cleaning methods can be used for electrodialysis and membrane capacitive deionization. Electrodialysis reversal provides an extra membrane cleaning possibility, next to the chemical cleaning procedures. By reversing the polarity the system, all charged particles are released from the membrane and removed in a waste stream. This procedure is used in almost all electrodialysis desalination plants, and has been very effective not only for the removal of precipitated colloidal material but also for removing precipitated salts (Strathmann, 2010).

3 Materials & methods

For the experiments two setups were used: a batch-operated electrodialysis unit and a laboratory scale research membrane capacitive deionization unit. Experiments were carried out in the laboratory of Voltea in Sassenheim. The water analyses were executed in the laboratory of Sanitary Engineering at the faculty of Civil Engineering. For the experiment with cooling tower blowdown water, water from the cooling towers of ELSTA was used.
In this chapter both experimental setups are described. Accordingly the chapter outlines which parameters were measured throughout the experiments and which parameters were measured in the water samples. In the last paragraph is explained how the two technologies are quantitatively and objectively compared based on the results of the experiment.

3.1 Electrodialysis

A 64002 ED cell (PCA GmbH, Germany) was used for the electrodialysis experiments. Between the cathode and the anode, 10 cell pairs of anion and cation selective membranes (8x8cm, standard PCCell GmbH reinforced membranes) and spacers (0.7mm) are arranged, providing a total membrane area of 0.13m^2. The membrane characteristics are given in Table 3-1. The cathode is made of V4A steel and the anode of Pt/Ir coated titanium. ED experiments were carried out in a batch configuration, meaning that the diluate, concentrate and electrolyte stream were recirculated in 2 litre jars during the experiment. The diluate and concentrate streams were pumped with a peristaltic pump (Masterflex 07528-10) at a constant flow rate of 0.024m/s, during all experiments unless otherwise indicated. The electrolyte stream, flowing in the electrode compartments, was pumped with a separate peristaltic pump (Masterflex 07554-85). For all experiments an electrolyte solution (2L) of 0.25M Na_2SO_4 was used for this purpose and recirculated with a flow rate of 0.36m/s. During the experiments all jars were mixed on a stirring plate to ensure the volumes were well mixed.

Table 3-1 PCCell membrane characteristics

	Permselectivity (%)	**Resistance (Ohm.cm^2)**	**Thickness (µm)**
PCCell AEM	88	1.08	180-220
PCCell CEM	91	0.95	160-200

Voltage and current over the cell was controlled with a power source (TRONIQ, PSU305D).The influence of the electrode reactions and the resistance of the electrodes itself was not negligible due to the small amount of cell pairs. Therefore a higher voltage over the cell was needed than actually was applied over the cell pairs. To measure this influence, electrodes in the form of a cupper screw were put into the tubing of the electrolyte stream; one close to the inlet and one close to the outlet of the ED unit. Both screws were connected with a wire to a voltage meter. The reading of this meter gave the electric potential over solely the cell pairs.

The conductivity was continuously measured in the diluate and concentrate streams with a multi-meter (WTW, multi 3420). Figure 3-1 shows the process and flow diagram of the experimental setup. Figure 3-2 gives and impression of the actual setup used.

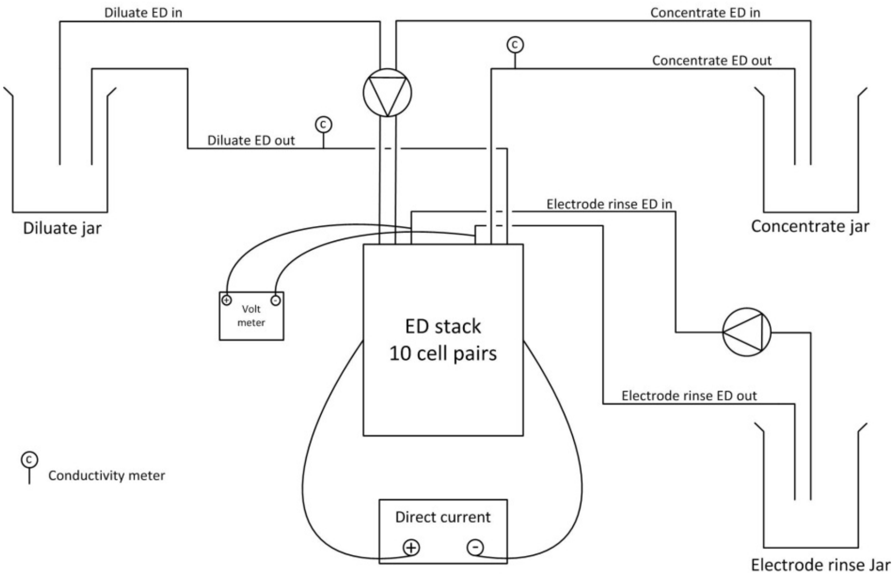


Figure 3-1 Process and flow diagram electrodialysis

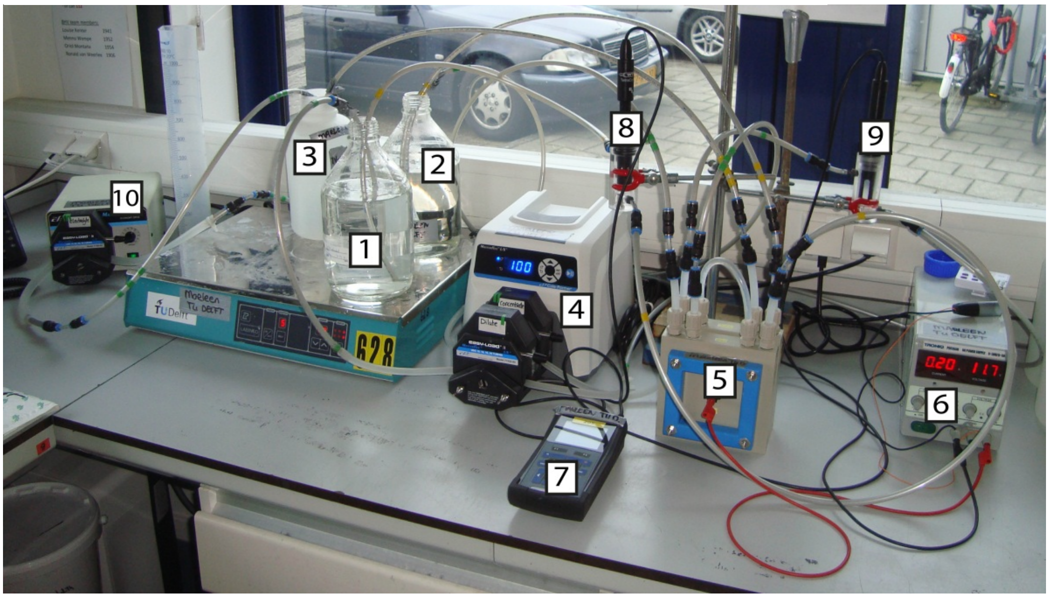


Figure 3-2 Electrodialysis experimental setup

1) *Diluate jar*
2) *Concentrate jar*
3) *Electrolyte jar*
4) *Peristaltic pump for diluate and concentrate stream*
5) *PCCell ED 64002 unit*
6) *Direct current*
7) *Conductivity meter*
8) *Flow cell influent diluate stream ED*
9) *Flow cell effluent diluate stream ED*
10) *Peristaltic pump for electrolyte stream*

3.1.1 Limiting current density

The limiting current density is the maximal current that can be transported by ions present in a certain water time, as presented in paragraph 2.2.5. The LCD was determined for all water types used in the ED experiments, according to the following procedure;

A volume of 2 litres of certain feed water was made up in a single jar. The diluate and the concentrate stream were both recirculated from this reservoir with a constant and similar flow, to ensure a constant quality of incoming water during the entire experiment. At the start of the experiment a constant current of 0.05 amperes was applied on the ED cell. The current was kept constant for a few minutes, after which it was increased in small steps and time intervals until the maximum voltage of 30V over the unit was reached. During each time interval, the voltage stabilized to a certain value for the corresponding applied constant current. Conductivity of the concentrate and diluate, and the voltage over the ED unit and the cell pairs, were measured continuously during the experiment.

The limiting current was determined from the obtained data by the method of Cowan and Brown (explained in paragraph 2.2.5) in which the resistance is plotted by the reciprocal of the current applied. The minimum in this graph is the limiting current density of a certain water type.

The limiting current was determined for all water types used during the experiments. NaCl solutions were prepared in different concentrations to investigate the influence of concentration on the LCD. Artificial water, similar to the CTBD water, was tested to determine the influence of certain ions on the LCD. For the CTBD water, limiting current density was investigated for undiluted water and for several dilutions (2, 4, and 8x). Dilutions, model waters and NaCl solutions were prepared with tap water. The CTBD water was filtered over a 10μm (nominal) cartridge filter. Due to the batch configuration of the ED setup, the LCD of dilutions of the CTBD water needed to be determined, as the diluate gets lower in concentration of ions during the experiment, which resulted in a lower LCD.

3.1.2 ED experiment with CTBD water

Batch experiments with ED and cooling tower blowdown water were carried out to investigate the effluent quality, energy consumption and membrane performance of the system. Therefore 10 experiments (=ten runs) with CTBD water were successively carried out. In each experiment 1L of pre-filtered CTBD water was put in the diluate jar and recirculated. For the concentrate stream a solution (0.5L) of 0.1M NaCl was prepared and recirculated during the experiment. A constant current of 0.15A was applied over the ED unit in each run and flows for both streams were kept equal. The experiments were carried out at room temperature. Clean membranes were used at the start of the experiments and the system and membranes were not cleaned between the 10 runs. The voltage profile of the clean membranes, and the used membranes after 10 runs was determined with a constant current experiment with 10mmol/l NaCl. During all the experiments, conductivity, voltage and time were measured continuously. Water samples were taken at the start and end of each run from the diluate and the concentrate volume.

3.2 Membrane capacitive deionization

A CapDI (Voltea B.V.) unit was used for the experiments with membrane capacitive deionization. Figure 3-3 shows the process and flow diagram of the MCDI process. Figure 3-4 gives and impression of the actual unit that has been used. Two stacks, each containing 23 cells ($A=1.12m^2$), were constructed and controlled by one operational unit. In one stack ion selective membranes similar to the membranes in the ED unit (PCCell, GmbH) were used. The cell pairs in the other stack were constructed with the ion selective membranes from Voltea. The membrane characteristics of both membrane types are presented in Table 3-2. Similar carbon electrodes (Voltea B.V.), spacers (0.1mm) and assembling materials were used for both stacks.

Table 3-2 MCDI membrane characteristics

	Permselectivity (%)	**Resistance (Ohm.cm^2)**	**Thickness (µm)**
PCCell AEM	88	1.08	180-220
PCCell CEM	91	0.95	160-200
Voltea AEM	92	0.35-0.4	78
Voltea CEM	96	0.7-1.1	26

Feed water was pumped from a reservoir through a cartridge filter (10µm nominal) and introduced into the MCDI stack. Constant current was applied during purification on both stacks until the maximum voltage was reached. Desalinated water was collected at the outlet. During wasting of the ions, the polarity was reversed and a constant current was applied over the stack, producing a brine stream at the outlet. A predictive model (Voltea B.V.) was used to determine the currents, flows and time intervals of the different phases needed for the desalination of different waters types to attain a required salt removal and water recovery. Flows and currents applied on the system were kept similar for both the stacks at all times.

The system operated fully automated and conductivities, pressure, current and voltage were measured continuously throughout the experiments. All the experiments proceeded for at least the operation of 20 stable cycles. Feed water of constant quality was fed into the system and water was not recirculated.

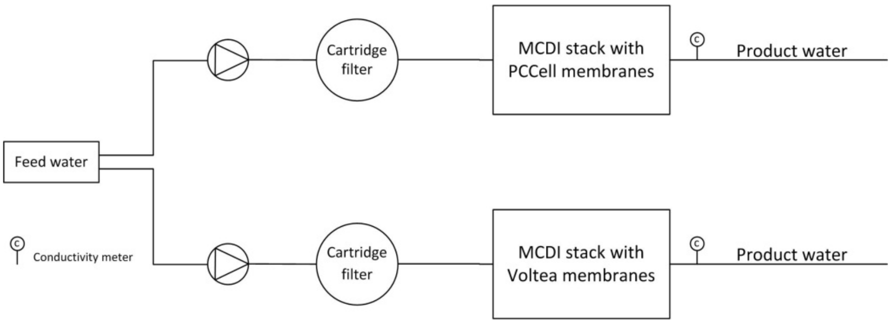
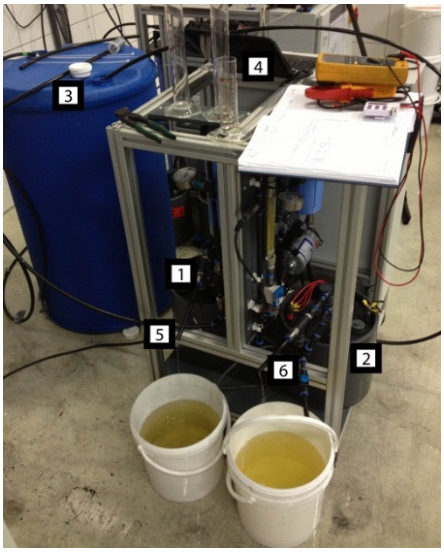


Figure 3-3 Process and flow diagram membrane capacitive deionization



1) *MCDI stack with PCCell membranes*
2) *MCDI stack with Voltea membranes*
3) *Feed water tank*
4) *Control panel*
5) *Outlet PCCell stack*
6) *Outlet Voltea stack*

Figure 3-4 Membrane capacitive deionization experimental setup

3.2.1 MCDI experiment with CTBD water

An 8h experiment was carried out with the MCDI unit to investigate the effluent quality, energy consumption and membrane performance of the system. A batch of 200L CTBD water of constant quality at room temperature was used. Flows, currents and time intervals were determined from the predictive model (Voltea B.V.) and are given in Table 3-3. The flow rate was checked by hand during the experiment at several times, because flows were too low to be recorded automatically. Samples for water analyses were taken from both stacks in the pure and waste phase, at different time intervals. The system was flushed before the start of the experiment to remove any materials from previous experiments. During the experiments the system and membranes were not cleaned. After the experiments the two stacks were opened up to investigate the membranes and spacers.

Table 3-3 MCDI operational parameters

	PCCell stack	**Voltea stack**
Flow rate pure (ml/min)	180	180
Flow rate in waste (ml/min)	90	90
Current in pure (A)	11.2	11.2
Current in waste (A)	20.0	20.0
Time interval pure (sec)	110	110
Time interval waste (sec)	85	85

3.3 Water analysis

Water samples were taken from both experiments for analysis of ion composition. Samples were taken for electrodialysis at the start en end of each batch experiment from the concentrate and diluate stream. For the MCDI experiment, samples were taken from both the purification and waste phase, at four different times (T1=start, T2=3h, T4=6h, T4=8h) throughout the 8h run with the CTBD water. All samples were stored in a fridge before analysing. pH and conductivity were measured of each sample with a multi-meter.

Ion chromatography was used to measure the following anions and cations: chloride, nitrate, phosphate, sulphate, sodium, potassium, magnesium, calcium, strontium and barium. Samples (10mL) were prepared at room temperature, by filtering them over a 0.45µm filter (Whatman, Germany) and measured in a 10x and 100x dilution. Ion standards (Sigma-Aldrich) were prepared in concentration of 0.1, 1, 10 and 50 ppm.

Total organic carbon (TOC) was analysed in all samples to study the amount of organic matter present in the water and to indicate any removal of organic matter by the technologies. TOC analysis was performed with a Shimadzu TOC analyser. Samples (30mL) were prepared in a 10x dilution after filtering them over a 0.45µm filter (Whatman, Germany). All samples were acidified with 1.4ml 1.0M HCL (Sigma-Aldrich).

3.4 Comparison procedure

Comparing ED and MCDI based on experimental results requires certain starting points for the experiments to make sure that the technologies are compared on an equal basis. It is essential to keep the fundamental principle of each technique as it is meant, and not to make the two technologies work exactly the same. The two starting points are:

- For the desalination of similar feed water both technologies need to desalinate the water down to a conductivity of 1000µS/cm.
- Water recovery for both systems is set at 66%. Water recovery is calculated according to the following equation:

$$Water\ recovery = \frac{V_{pure}}{V_{feed}} * 100\% \qquad (4)$$

in which V_{feed} is the sum of the desalinated water produced plus the waste stream created for each technology. Furthermore, temperature and other influential parameters were kept as similar as possible during all experiments.

The experimental results of the experiment with CTBD water of both technologies were evaluated and compared based on the criteria outlined below;

Overall performance

First of all, it was determined whether electrodialysis and membrane capacitive deionization reach the required desalination rate and water recovery.

Energy consumption

For both technologies, it was calculated how much energy was needed to treat a certain volume of water. To investigate the influence of salt concentration on energy consumption, different water types were tested on both technologies. The required energy was calculated from the average voltage profile and the applied constant current per cubic meter.

Current efficiency

Current efficiency is a measure of how efficient ions are transported across the ion exchange membranes for a given applied current. Current efficiencies were calculated based on the ion concentrations measured in the samples taken during the experiment. The sum of current efficiencies for all anions and all cations can both be maximal 100% which indicates a fully efficient system. By comparing the current efficiencies of ED and MCDI, and both membrane types, it can be indicated which system uses the current more efficiently. Current efficiencies of application of ED membranes in the MCDI were compared to the current efficiencies of the ED. Current efficiencies were calculated according Equation 1 and 3.

Ion removal

Ion concentrations were measured in the water samples taken from each experiment. Ion removal is the ratio between the ion concentration present in the feed water and in the desalinated water and can be calculated according to the following Equation 5. ED and MCDI were compared based on ion removal to see whether the preference of ions and the removal was similar or in what type of ions they are different.

$$Removal\ (\%) = \frac{c_{feed} - c_{diluate}}{c_{feed}} * 100 \tag{5}$$

Membrane and spacer performance

The membrane performance was determined by measuring the permselectivity and resistance of clean membranes and the membranes used after the experiment. The determination of these parameters was done by the analytical team of Voltea B.V. according to the following procedure;

Permselectivity

The experimental set up for the determination of membrane permselectivity consisted of two cells separated by the membrane under investigation. On one side of the membrane a 0.05M KCl solution was pumped through the cell and on the other side a 0.5M KCl solution. Two reference electrodes were placed into the solution on either side of the membrane and they were used to measure the potential difference over the membrane.

Resistance

The set up to measure the resistance of the membranes consisted of two cells separated by the membrane. A solution of NaCl 2M was pumped in the compartments, and the difference of resistance in both sides of the membrane was measured by platinum electrodes. An alternating current was used. A blank reading (with no membrane) was taken before each membrane reading. Membrane resistance was calculated subtracting the membrane resistance and the resistance of the solution (blank).

Furthermore was soft data obtained by inspecting the membranes and spacers on colour changes, structure and visible scaling and fouling. Pictures were taken from the membranes, spacers and electrodes before and after the experiments to present visible effects.

3.5 Experimental overview

The experimental work is summarized in the figure below which shows all the different experiments and their mutual relation.

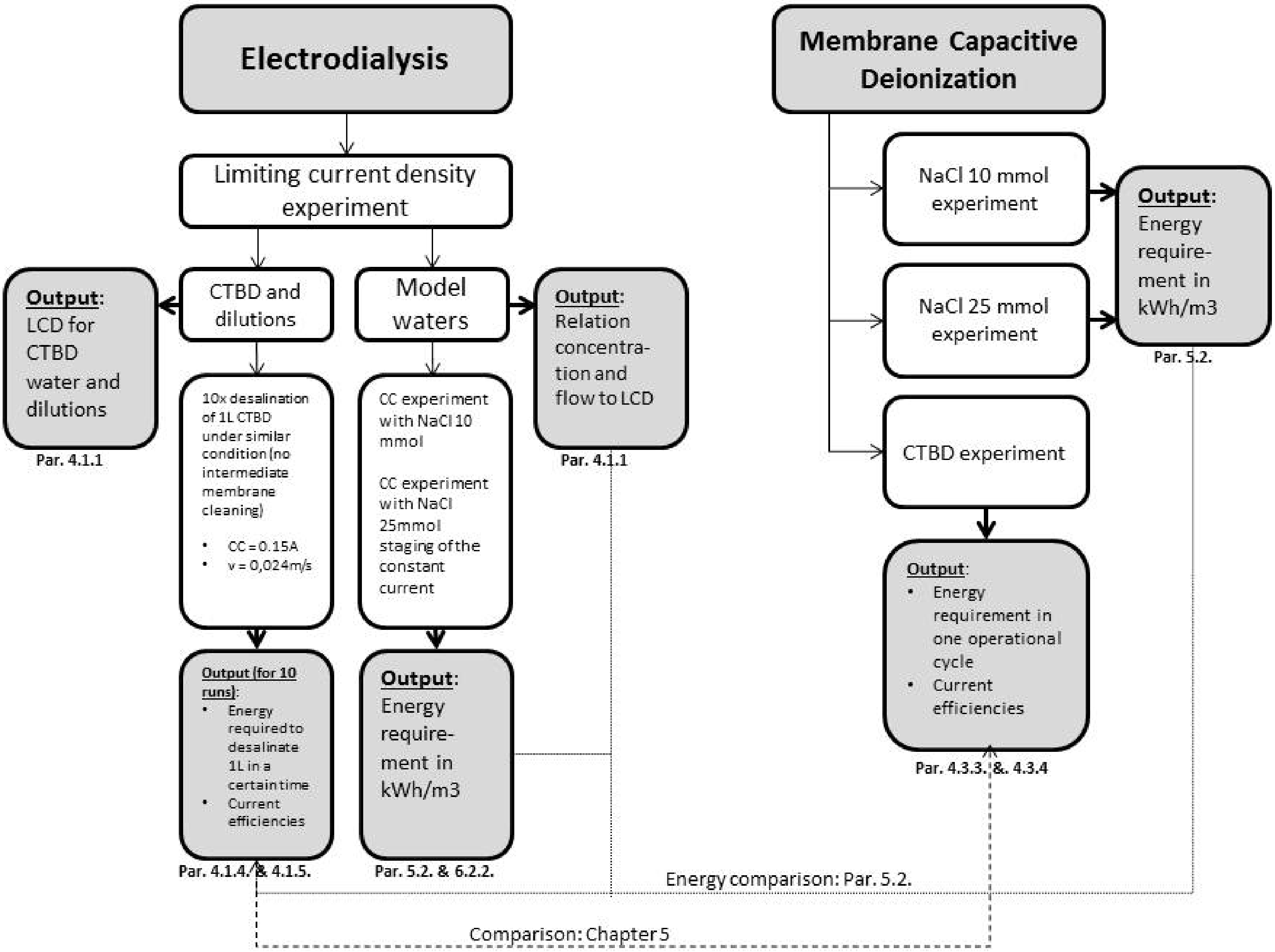


Figure 3-5 Experimental overview

4 Results and discussion per technology

In this section the results of the experiments are presented for each technology. First the findings for electrodialysis are given starting with the investigation of the limiting current density. Secondly, the results of the experiments with CTBD water are shown; presenting the conductivity profile and ion removal, energy consumption and current efficiencies and finally the membrane performance. The section continues with the results of the experiments with MCDI. Results are again discussed in the following sections: conductivity profile and ion removal, energy consumption and current efficiencies and membrane performance. Both result sections are concluded with a discussion on the results of the technology. The comparison of the two technologies and the discussion of the results are presented in Chapter 5.

4.1 Electrodialysis

4.1.1 Limiting current density

The limiting current density was determined in different experiment for several water types.

ELSTA CTBD water

Limiting current densities were determined for different feed waters by plotting the overall resistance versus the reciprocal of the current density. The minimum value in this graph is derived by taking the lowest point in the graph and presents the limiting current density of a certain water type. Figure 4-1 shows the LCD for ELSTA CTBD water and several dilutions of this water.

Table 4-1 presents the LCD derived from this figure and the corresponding conductivities. These results show that the LCD decreased with increasing dilution factor. The four times diluted water gave a deviating result as it does not match in the decreasing trend of the LCD with decreasing ion concentration.

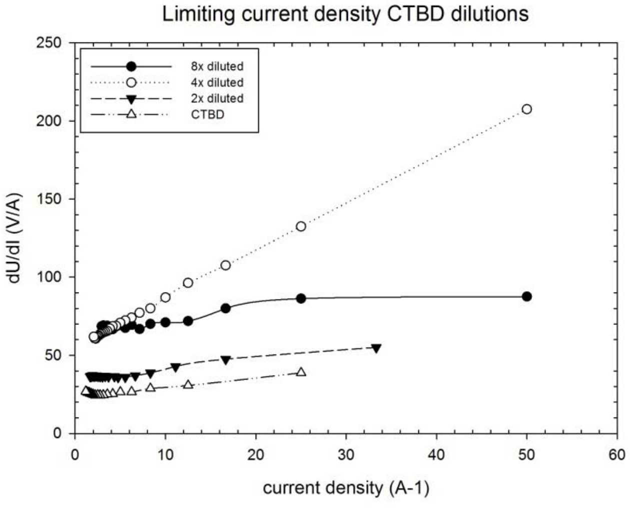


Figure 4-1 Limiting current density of CTBD water at various concentrations

Table 4-1 Limiting current densities of cooling tower blowdown dilutions

Water type	**Conductivity (mS/cm)**	**Limiting current density (A/m^2)**
CTBD	3.9	56.3
CTBD 2x diluted	2.16	32.8
CTBD 4x diluted	1.4	68.8
CTBD 8x diluted	1.01	21.9

Influence of concentration and flow rate on LCD

Experiments have been carried out in order to investigate the relation between the LCD and salt concentration. For this experiment the LCD of eight different sodium chloride solutions was determined. Figure 4-2 shows a summary of the experiments by plotting the NaCl concentration against the LCD. This gives a linear relation between the two parameters. The LCD increased with increasing concentration of sodium chloride. The plot of the overall resistance against the reciprocal of the current density for all eight NaCl concentrations is presented in Appendix B.

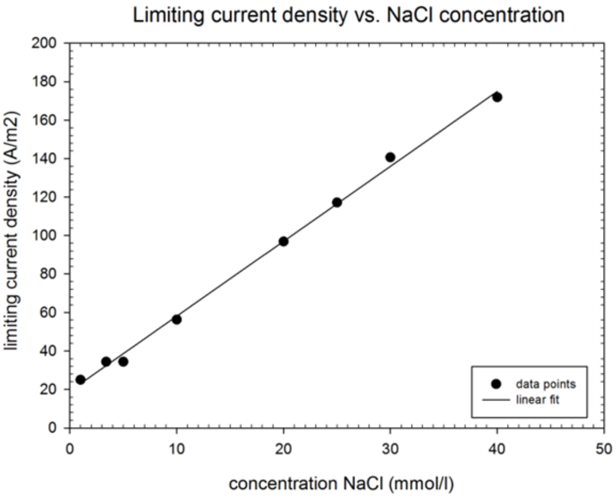


Figure 4-2 Relation limiting current density and NaCl concentration

Figure 4-3 presents a linear relation between the LCD and the velocity through the ED stack, for four different velocities. With increasing velocity, there is more turbulence at the membrane surfaces, and a higher mass transfer rate of ions in the vicinity of the membrane. As such, ions were transported faster towards the membranes, resulting in higher limiting current densities possible. The individual graphs of the overall resistance against the reciprocal of the current, of the four runs are presented in Appendix B.

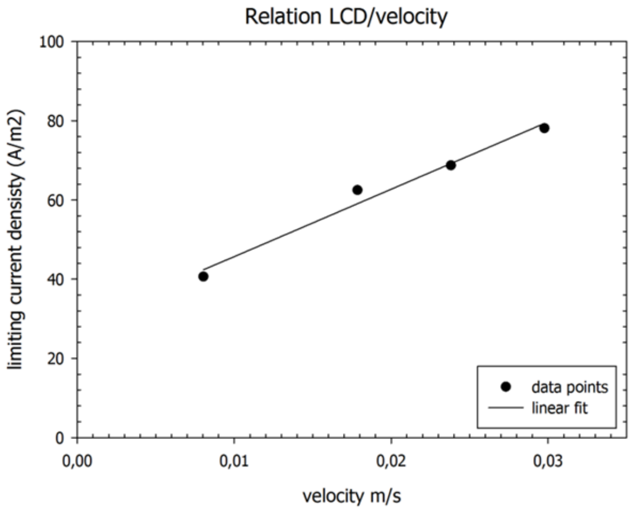


Figure 4-3 Relation limiting current density and flow rate

Limiting current density of model waters

Limiting current densities of different artificial water with similar salt concentrations as in the CTBD water, have been researched in order to study the influence of certain ions on the LCD. Sodium, chloride, calcium and sulphate are the ions with the highest concentrations in CTBD water. All are present in a concentration of around 12mmol/l (see Table 2-1). Table 4-2 shows the LCD and the feed conductivity of the different artificial waters tested. The results show that the LCD of the CTBD water was equal to that of model water with 12mmol/l sodium sulphate (Na2SO4) and calcium chloride ($CaCl_2$). The LCD of Na_2SO_4 and $CaCl_2$ and, both consisting of a mono- and divalent ion were almost equal. The LCD of NaCl was lower compared to the other salts; however they were all higher than the LCD of the CTBD and artificial CTBD water. In Appendix B is the graph given for the determination of the LCD of the different waters.

Table 4-2 Limiting current density of various water types

Water type	Conductivity (mS/cm)	Limiting current density (A/m^2)
12mmol/l $CaCl_2$ (+demi water)	2.3	100
12mmol/l Na_2SO_4 (+demi water)	2.2	84.4
12mmol/l NaCl (+demi water)	1.8	65.9
12mmol/l Na_2SO_4 + 12mmol/l $CaCl_2$ (+demi water)	3.8	56.3
ELSTA CTBD	3.9	56.3

4.1.2 Conductivity profile

Conductivity of the concentrate and diluate leaving the ED unit to the batch reservoir were measured continuously during the experiment. The conductivity in the diluate decreased during the experiment and the concentration of the concentrate increased, as shown in Figure 4-4 and 4-5. The two main observations in these two graphs are that it took on average 50 minutes to desalinate 1L of CTBD water down to a conductivity of 1000µS/cm with the set operational conditions. The other observation is that the conductivity profile of all runs, of both diluate and concentrate, started on the same value but deviated towards the end of the experiments.

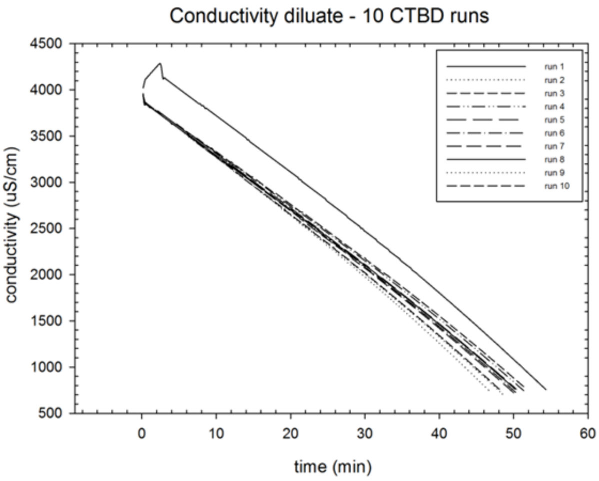


Figure 4-4 Conductivity profile diluate – 10 CTBD water runs

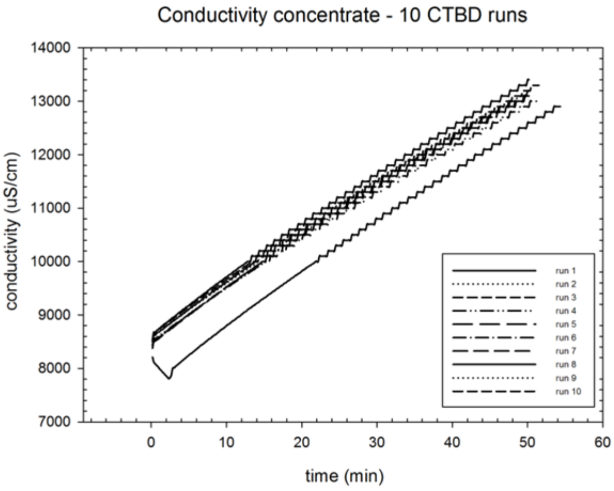


Figure 4-5 Conductivity profile concentrate – 10 CTBD water runs

4.1.3 Ion removal

Ion removal was studied by measuring the concentrations of ions in the different water samples. In Figure 4-6, the ion removal from the diluate (start concentration diluate – end concentration of the diluate), is plotted next to the ion uptake in the concentrate (the end concentration concentrate – the begin concentration of the concentrate). Results are given for the 7th run with CTBD water because these results showed an average result for all the ten runs. Concentrations are expressed in mmol/l. This graph shows that removal of nitrate, phosphate, sulphate, potassium and magnesium was almost equal to the uptake. For calcium, the uptake was 2mmol/l lower than the removal.

Sodium and chloride show deviating results. They both have a negative result for uptake, which indicates that fewer ions were taken up by the concentrate stream, than were removed from the diluate stream. This is very unlikely to have happened because the diluate showed that there was removal of sodium and chloride. So these ions should have moved towards the concentrate stream as they cannot disappear from the total water volume.

Figure 4-7 and 4-8 present the trend of percentage cation and anion removal from the diluate over the 10 runs. Both graphs show clearly that a constant removal of ions was achieved over the 10 runs. Sulphate and nitrate are anions which were more removed compared to the other anions. The preferential cation was potassium which was removed for 93%. The other cations were also removed over 70%. Barium and strontium were analysed in the ion chromatograph but concentration were below the detection limit.

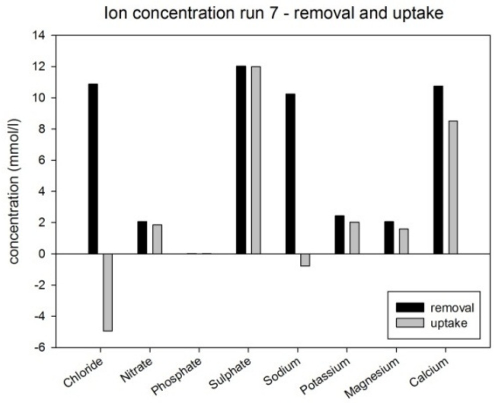


Figure 4-6 Ion balance – CTBD water run 7

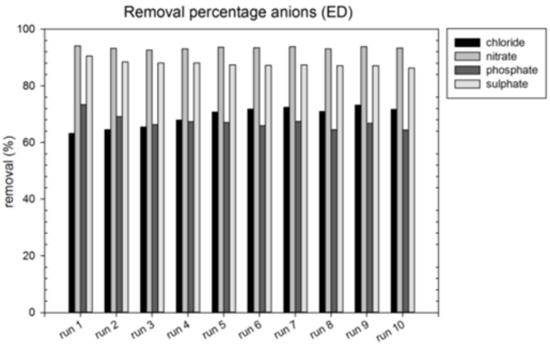


Figure 4-7 Removal percentages of anions in ED

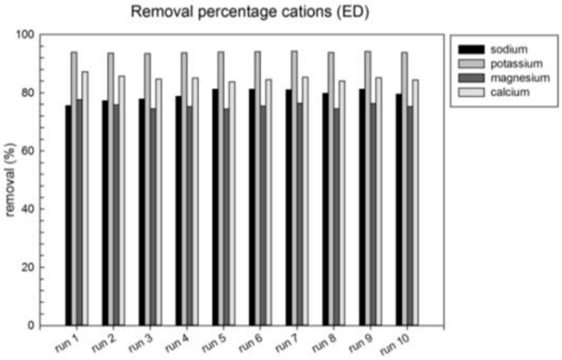


Figure 4-8 Removal percentages of cations in ED

4.1.4 Energy consumption

During the ten runs with CTBD water, the voltage was measured over the entire ED unit and over the cell pairs. Figure 4-9 shows the voltage profile across the cell pairs for all runs. The results show an increase of resistance in time during desalination of the batch feed water for all runs. Moreover is it clear that the voltage profile increased over the first four runs, where after it stabilised. The minimal and maximal energy requirement was calculated from the graph by multiplying the average voltage with the constant current of 0.15A. To desalinate 1L of CTBD water in 50 minutes with a batch ED configuration, 0.38kWh/m^3 (minimum) to 0.44kWh/m^3 (maximum) of energy input was needed. Further calculations on energy requirements are given in Chapter 5.

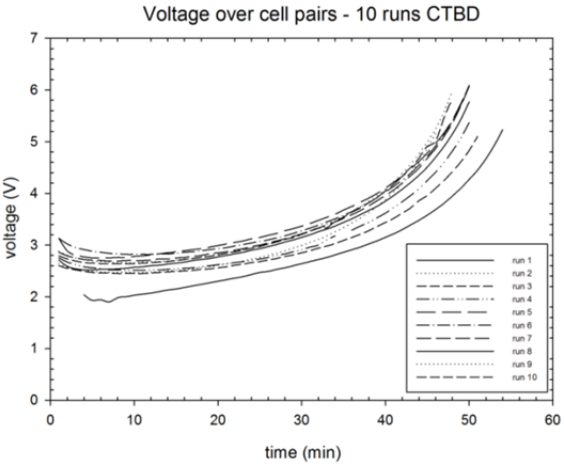


Figure 4-9 Voltage profile 10 CTBD water runs

4.1.5 Current efficiencies

Current efficiencies were calculated for each run with CTBD water and were calculated from the ion concentrations measured in the water samples. Figures 4-10 and 4-11 present the current efficiencies for the major cations and anions. The figures also indicate to which extent the different ions contributed to the current efficiency. The efficiency for anions reached an average of about 85% for the 10 runs. It is also clear that large part of the current used, was attributed to the divalent ion sulphate, followed by monovalent ion chloride. The efficiency for cations was on average 88% for the 10 runs. The divalent ion calcium attributed for a large part to the efficiency, followed by the monovalent ion sodium. Both anions and cations gave fairly constant current efficiencies over the series of 10 runs.

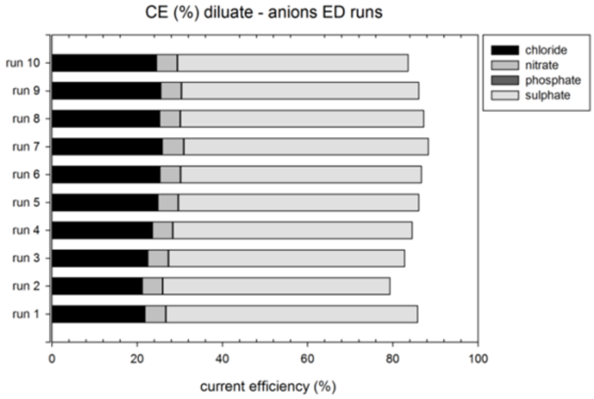


Figure 4-10 Current efficiencies diluate– anion

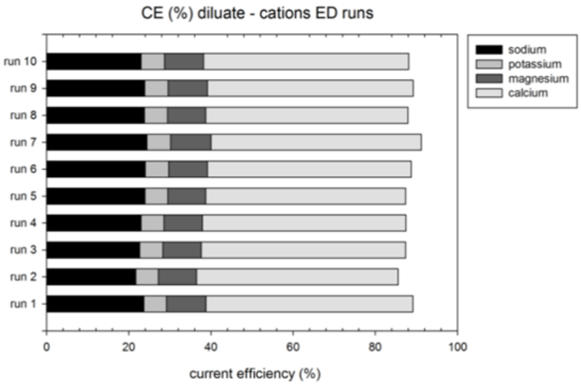


Figure 4-11 Current efficiencies diluate– cation

4.1.6 Membrane analysis

TOC balance

Concentrations of TOC in the feed water (73mg/l) were constant for all 10 runs. TOC was analysed in all water samples to see whether the organic matter passed through the ion selective membranes or whether it was retained on the membranes or spacers. A TOC balance was made based on these measured concentrations and Figure 4-12 shows the deficit in this balance over the 10 runs with CTBD water. The graph shows a clear decline which indicates that with passing the runs, less TOC was retained on or in the membranes and almost all TOC passed the ED stack without being retained on the membrane.

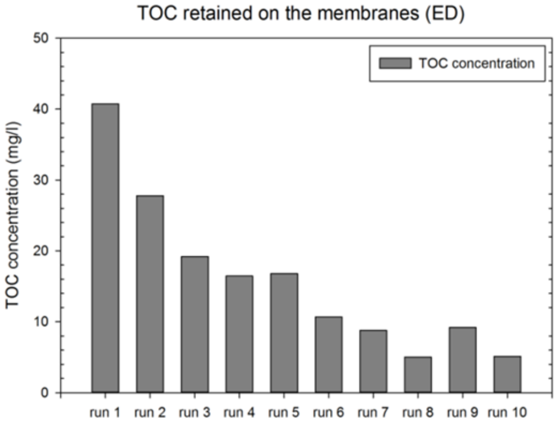


Figure 4-12 TOC retained on ED membranes

Membrane autopsy

The ion selective membranes were compared before and after the experiments by taking pictures and by measuring the permselectivity and resistance of the membranes. Pictures of the membrane analysis are presented below. A brown colour was clearly visible on the anion selective membrane indicating severe fouling of the membranes, most probably by organic matter. The CEM did not show significant discolouration. On the cathode small amount of little white particles were visible after opening up the unit. On the spacers, no significant fouling or other effects were visible.

Figure 4-13 Clean AEM electrodialysis

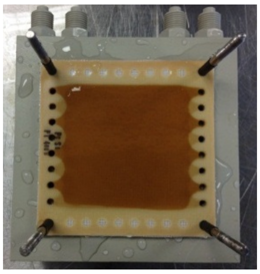


Figure 4-14 Used AEM electrodialysis

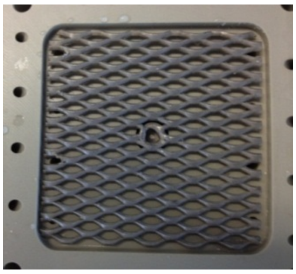


Figure 4-15 Anode electrodialysis cell

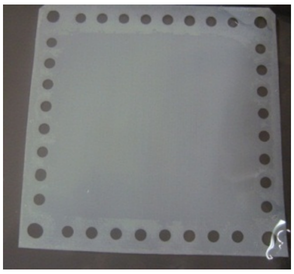


Figure 4-16 Clean CEM electrodialysis

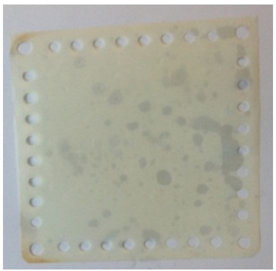


Figure 4-17 Used CEM electrodialysis

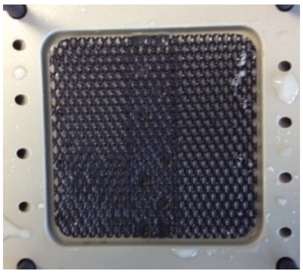


Figure 4-18 Cathode electrodialysis cell

Resistance and permselectivity of the membranes was determined before and after the experiment with the CTBD water. Table 4-3 shows the results of these analyses. It is clear that the resistance of the AEM and CEM has increased due to desalination of CTBD water. The permselectivity of AEM membranes decreased, whereas it of the CEM increased. This is very unlikely to have happened, since membranes tend to degrade when being used. It should be remarked that this difference was probably due to differences in batch of both membranes. The values for clean membranes were determined from the membrane batch used for the membranes in the MCDI, so characteristics can be slightly different.

The membranes of the electrodialysis setup were cleaned between each experimental series and resorted to almost their original capacity. The cleaning procedure and the methods which were used to determine whether the capacity was restored, are presented in Appendix C.

Table 4-3 Membrane permselectivity and resistance of PCCell membranes

	Permselectivity (%)		**Resistance (Ohm.cm^2)**	
Membrane	AEM	CEM	AEM	CEM
PCCell new	88	91	1.08	0.95
PCCell used	78	95	1.13	1.15

4.2 Discussion results electrodialysis

The limiting current density is a determining factor in the operation of an ED, and results show that the LCD of undiluted CTBD water was 56.3A/m^2. This is a fairly low limiting current density compared to LCDs found for NaCl solution (Lee, 2006). The 4x diluted water did not meet with the expected increase of LCD with decreasing salt concentrations. Dilutions of the CTBD water were made up with tap water, by which some extra ions present in this tap water, were introduced to the dilution series. This might have had an effect on the results and be an explanation for the deviating result for the 4x dilution. Moreover, the graphs do not always show an explicit minimum, which can be related to the fact that the voltage over the ED stack should during all experiments not exceed 30V. The LCD of certain waters might only be reached at the end of the experiment when the voltage was already quite high. This resulted in an unclear and multiple minima in the plot. The LCD was in these situations chosen as the first minimum derived from the data.

From the LCD results with artificial CTBD water, it can be concluded that sodium, calcium, sulphate and chloride were the ions of determining influence on the LCD. The LCD for artificial CTBD water was found to be the same as the real CTBD water (56.3A/m^2). The results in Table 4-2 show that the LCD of artificial blowdown water was almost twice as low as compared to the LCD of solely Na_2SO_4, $CaCl_2$ and NaCl in a 12mmol/l concentration. This difference can be attributed to the fact that the solubility product of $CaSO_2$ was exceeded. With a concentration of 12mmol/l Na_2SO_4 and 12mmol/l $CaCl_2$ the present concentration was $1.44 * 10^{-4}\ mol^2/l^2$, which is larger than the solubility product of $CaSO_2$ $4.93 * 10^{-5}\ mol^2/l^2$, thus there was precipitation of calcium sulphate which decreased the available amounts of ion and thus was the LCD lower for this water. The linear relation found between the LCD and the ion concentration and the flow rate is in agreement with the results of Lee et. al (2005).

Experimental setup

Low limiting current densities result in a large requirement in membrane surface area needed to desalinate water and hence, high costs for membrane investment (Strathmann, 2004). The influence of temperature was not taken into account during the experiments. The feed water was not conditioned and during the experiments the water temperature increased a couple of centigrade. This temperature shift might have had an influence on the results (Xutoi, 1983).

Experiments were carried out with a constant current below the limiting current density of the end water quality with conductivity <1000µS/cm. At the start of each experiment, the salt concentration in the diluate steam was high (3900µS/cm), and much lower constant current was applied than the limiting current of this water. It resulted in a longer time needed to desalinate the water at fairly low energy consumption. This is a consequence of operating the experimental setup in a batch configuration. In practice this can be balanced by applying different stages of ED stacks (Tsiakis, 2004). Water then flows through several stacks to reach the required product water quality. Each successive stack can be operated with a lower constant current to make an energy efficient system.

Ion removal and membrane performance

The removal rate of ions was constant over the 10 runs with CTBD water, as shown in Figure 4-9 and Figure 4-8. Combining these results with the, likely organic, fouling on the membranes as obtained from the TOC analyses, suggests that the ion removal was not influenced by the membranes fouling. With the fouling of the anion selective membranes the resistance increased, as shown by increasing voltage over the first couple of runs, but ion removal remained constant. When the TOC fouling stabilized, it was observed that half of the organic matter remained in the diluate stream, whereas the other half passed through the membrane and ended up in the concentrate. It should be noted that these results were based on 10 short batch experiments with 1L of CTBD water. Nothing can be said about effects on larger scale and longer term.

Considering the fouling of the membrane, the AEMs fouled severely by most likely negatively charged organic matter, whereas CEMs were not visibly affected. The fouling also affected the deterioration of the membranes which is presented in Table 4-3. It is likely that the pores of the membranes blocked, which increased the membrane resistance. Thus anion selective membranes degraded more than cation selective membranes, which is in line with previous research on ion selective membrane fouling by Lindstrand et al. (2000).

The results for the ion balance gave unexpected values for sodium and chloride. Concentrations in the concentrate were lower at the end of the experiment compared to the beginning, where an increase was expected due to ion removal from the diluate, as also shown in Figure 4-6. The difference might be attributed to the water transport. Since concentrations are very high, little transport can account for a large shift in concentration. Moreover, the start concentration of the diluate (100mmol/l NaCl) was much higher than the removed concentration (ca. 9mmol/l NaCl). Measurement of the ion concentration in the concentrate samples were carried out twice. Both analyses showed similar results which make it very unlikely that errors were made in preparing the samples for the ion chromatograph.

pH was measured for all water samples but did not give any unexpected results, so therefore these values are not given in the results section.

4.3 Membrane capacitive deionisation

4.3.1 Conductivity profile

The conductivity profile of the two MCDI stacks is shown in Figure 4-19 for five average cycles, throughout the 8h experiment. Both stacks showed a sharp conductivity increase during the waste phase and a stable plateau at ca. 1000µS/cm during the purification phase. The profile of the PCCell membranes reached a slightly higher conductivity in purification and lower conductivity during the wasting phase, compared to the Voltea membranes. The graph also shows that during one cycle the conductivity was about half the time 1000µS/cm or slightly below that. The average water recovery over the whole experiment was for the PCCell membranes 40% and for the Voltea membranes 62%. This means that a water recovery of 66%, which was set as a requirement, was not met. Stable operation conditions were achieved in 100 cycles.

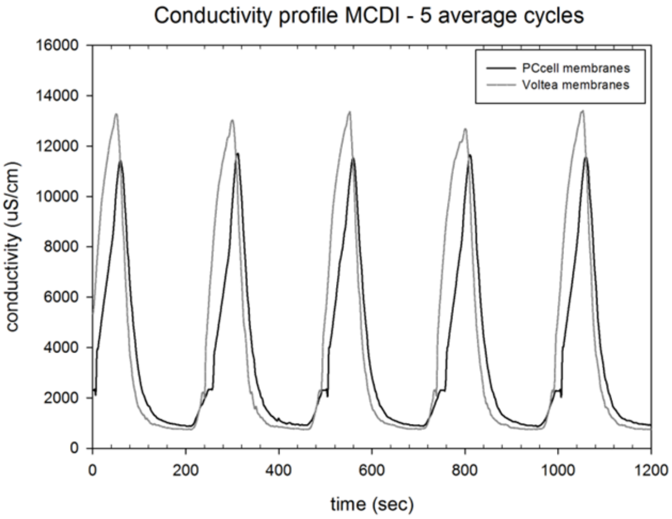


Figure 4-19 Conductivity profile of PCCell and Voltea membranes of in 5 average cycles

4.3.2 Ion removal

Ion removal was studied by the concentrations of ions measured in the different water samples. Figure 4-20 and 4-21 present the trend of percentage cation and anion removal over the whole experiment. Both graphs show clearly that a constant removal of ions was achieved and that this removal was slightly higher for the Voltea membranes. Chloride and nitrate were the preferential anions for removal in both stacks. Potassium was the preferential cation for the Voltea membranes, whereas no cation was specifically better removed for the PCCell membranes. Overall removal rates of the ions were 60% or higher. Barium and strontium were analysed in the ion chromatograph but concentrations were below the detection limit.

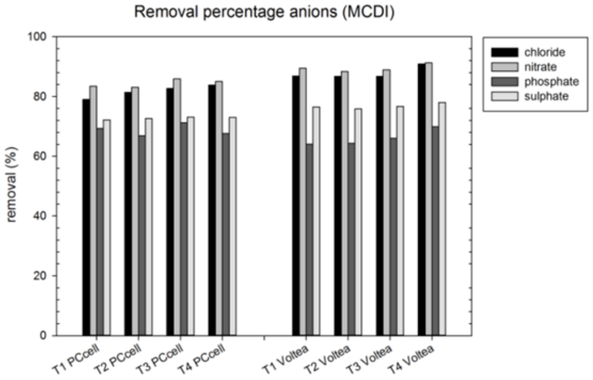


Figure 4-20 Removal percentages of anions in MCDI

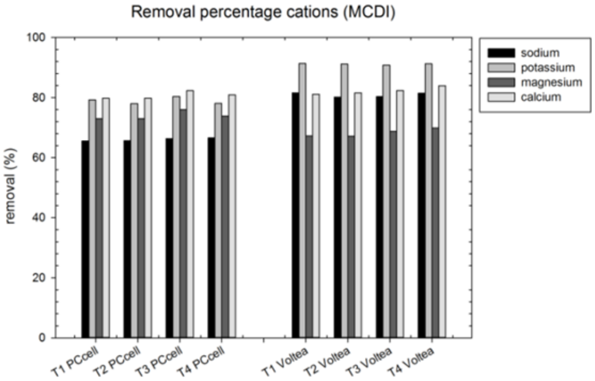


Figure 4-21 Removal percentages of cations in MCDI

4.3.3 Energy consumption

Applying constant current resulted in an increase of voltage when fouling/resistance is built up on the membranes. The voltage over the 2 stacks was measured throughout the whole experiment with CTBD water. Figure 4-22 presents the voltage profile of the two stacks over 5 average cycles. The figure shows a similar profile for both membranes. The small peak at the start of each cycle is the voltage during the waste phase. The part of the graph where the voltage increases from ca. 1V to 1.5V is the purification phase.

It was calculated from this graph that on average 2.1kWh/m^3 was needed for each stack, in one operational cycle, in which about 330ml of desalinated water was produced. Energy consumption of MCDI is further elaborated in Chapter 5.

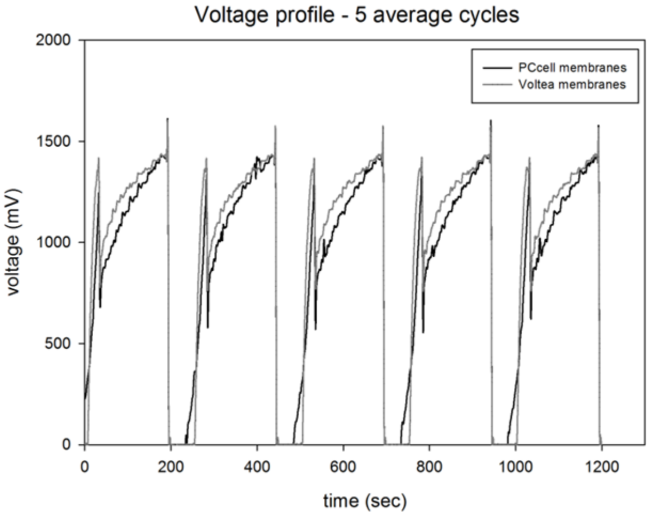


Figure 4-22 Voltage profile of PCCell and Voltea membranes of in 5 average cycles

4.3.4 Current efficiencies

Current efficiencies were calculated for the purification phase of the MCDI from the ion concentrations measured in the water samples. Figure 4-23 and 4-24 present the current efficiencies for both cations and anions for the two membrane types and for the four different time steps. The figures also indicate to which extent the different ions attribute to the current efficiency.

The efficiency for anions was on average 58% for the Voltea membranes and 55% for the PCCell membranes. It is also clear that large part of the current use was attributed to the divalent ion sulphate, followed by monovalent ion chloride, for both membrane types. The efficiency for cations was on average 63% for the Voltea membranes and 60% for the PCCell membranes. Here, the divalent ion calcium contributed for a large part to the efficiency, followed by the monovalent ion sodium. Both anions and cations presented fairly constant current efficiencies over the 8 hour run.

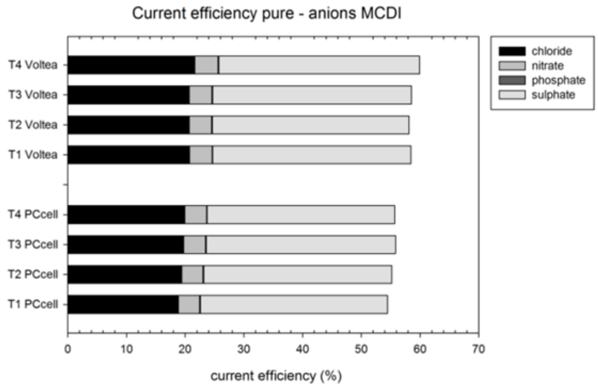


Figure 4-23 Current efficiencies during pure – anion

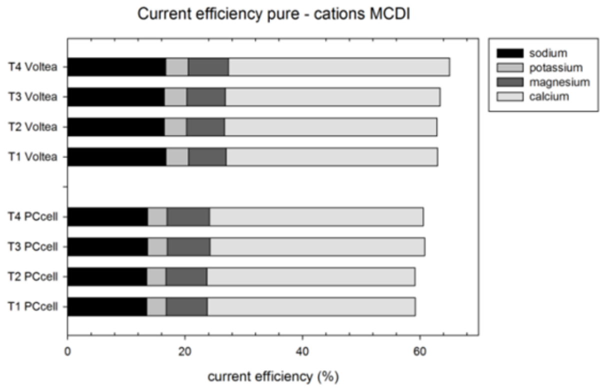


Figure 4-24 Current efficiencies during pure – cation

4.3.5 Membrane analysis

TOC balance

TOC concentration in the feed water was around 73mg/l throughout the experiment. TOC was analysed in pure water samples to see if any TOC removal occurred during the desalination phase. Concentrations were also measured in the waste samples to determine whether TOC was released from the membranes and electrodes during reversed polarity. Figure 4-25 shows the TOC concentrations in the different samples, for both Voltea membranes and PCCell membranes. Pure and waste relate to the operation phase of the system, T1 to T4 refers to the time step. The graph shows that there was little TOC removal in the purification phase and some TOC release in the waste phase. However, differences were minor and could also be due to inaccurate sampling. Overall it can be said that there was limited TOC removal by MCDI, and that concentrations in the effluent were fairly constant. So there was also limited TOC on or in the membranes.

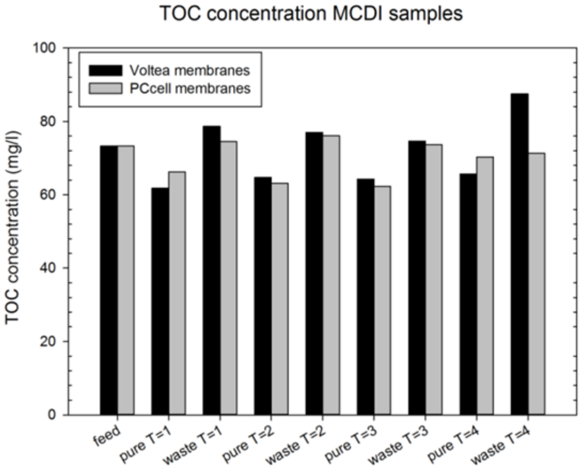


Figure 4-25 TOC concentration in water samples MCDI

Membrane autopsy

The ion selective membranes were compared before and after the experiments by taking pictures and by measuring the permselectivity and resistance of the membranes. Pictures of the membrane, spacer and electrode analysis are presented below for both PCCell and Voltea membranes. It is clear from the pictures that there was change in colour of the AEMs; both membranes types were more brownish compared to the clean AEM. The CEM's did not change significantly in colour during the experiment. Limited scaling was observed for both stacks on the edges of the spacers where the water was introduced in the stacks. The electrodes of the Voltea stack showed little scaling, compared to the PCCell electrodes which had more serious scaling, as can be seen in Figure 4-30 and 4-31. All spacers were free of serious particle deposits.

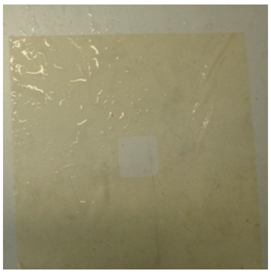


Figure 4-26 Clean AEM Voltea MCDI stack

Figure 4-27 Used AEM Voltea MCDI stack

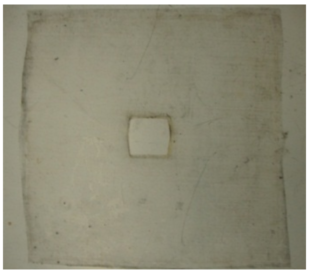


Figure 4-28 Spacer used in Voltea MCDI stack

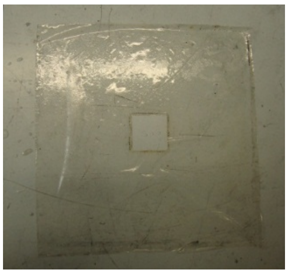


Figure 4-29 Used CEM Voltea MCDI stack

Figure 4-30 Carbon electrode used in Voltea MCDI stack

Figure 4-31 Carbon electrode used in PCCell MCDI stack

Figure 4-32 Used AEM PCCell MCDI stack

Figure 4-33 Used CEM PCCell MCDI stack

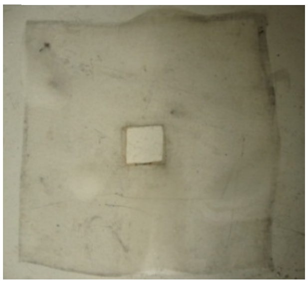


Figure 4-32 Spacer used in PCCell MCDI stack

Resistance and permselectivity of all membranes was determined before and after the experiments. Table 4-4 shows the results of these analyses. It is clear from the table that the AEM membranes of both PCCell and Voltea increased in resistance and decreased in permselectivity after the experiment. The CEMs showed less degradation for both membrane types. The resistance of the Voltea CEM even seems to have decreased, which is very unlikely. This difference can again be attributed to the fact that values for clean membrane tests were determined from a different batch than the actual membranes used during the experiments.

Table 4-4 Membrane permselectivity and resistance of MCDI membranes

	Permselectivity (%)		**Resistance (Ohm.cm^2)**	
Membrane	AEM	CEM	AEM	CEM
Voltea new	92	96	0.3	0.7
Voltea used	86	96	0.56	0.66
PCCell new	88	91	1.08	0.95
PCCell used	95	91	1.32	0.77

4.4 Discussion results membrane capacitive deionisation

Both membrane stacks did not reach the required water recovery of 66%. In addition, the average conductivity in the purification phase for the PCCell membranes was most of the time higher than the required 1000µS/cm. This contrasts with the Voltea membranes that did reached a conductivity lower than 1000µS/cm during the purification phase. The difference in conductivity profile between the two membrane types, as shown in Figure 4-19, can be attributed to difference in membrane characteristics. PCCell membranes are thicker which results in a larger distance between the electrodes, this means that the distance between the electrodes is larger and that a stronger electric field is needed to transport the ions. Next to that, the resistance of the unused PCCell CEM is about three times higher than that of the Voltea CEM. This means that a higher voltage is needed to transport the ions through the CEM. However, this voltage difference was not observed, thus less ions were removed which resulted in a higher conductivity of the purified water. No explanation was found for the voltage not being higher for PCCell membranes as expected. Also the lower selectivity of the PCCell membranes compared to the Voltea membranes can account for the difference in conductivity of the product water.

Operational aspects

Feed water, flows, currents and other conditions were similar for both systems during the experiment, so they were not of influence on the salt removal. The operation of the MCDI unit was limited by current which could be maximal 20A due to settings in the stack. Because of the high salt concentrations, flows had to be very low to reach the required desalination rate.

Current efficiencies of 50% and 60% were measured. This is a low efficiency compared to the high efficiencies (up to 97%) MCDI claims to work at (Biesheuvel, 2010). The differences in current efficiencies and ion removal can partly be attributed to impurity of the water samples. Due to the low flows, water samples had to be taken during almost the whole cycle to get enough volume. The conductivity profile shows that, especially during waste, the conductivity did not stabilize. This means that the samples that were taken were a mixture of water over a certain time period and were therefore not very accurate.

Ion removal and membrane performance

Differences in membrane and electrode performance between the two stacks with different membrane types were observed. The electrodes of the PCCell stack showed some scaling which can be attributed to insufficient compression of the membranes. This results in possible bypassing of the water, and therefore decreasing the salt removal efficiency. The PCCell membranes are reinforced and thicker compared to the Voltea membranes. This means that the distance between the electrodes is larger and that a stronger electric field is needed to transport the ions. Scaling was not observed on the Voltea electrodes. The two membranes types also preformed differently in ion removal. Voltea membranes gave higher ion removal rates, but this result was, again, not completely representative due to the impurity of the water samples. The membranes have a preference for chloride and nitrate, which ion size are both small compared to the other ions, and therefore passed more easily through the membranes. Figure 4-21 suggests that magnesium was better removed by the PCCell membranes, whereas sodium was better removed with the Voltea membranes.

AEM's in both stacks decreased in permselectivity and increased in resistance after the experiments. Increase in resistance is likely to be attributed to blocking of the membranes by small particles and fouling. Results show a decrease in resistance of the CEM's after the experiments. This is very unlikely and might be due to small failures (e.g. flaws) in the membranes during the analysis of the membrane. Furthermore, the data of the clean membrane measurements for Voltea membranes was obtained from another batch than the batch used during testing. Overall, the AEM's degraded more in performance than the CEM's, which is according to literature (Lindstrand et al., 2000). TOC was not removed in desalination with MCDI as presented in Figure 4-25.

pH was measured for all water samples but did not give any unexpected results, so therefore these values were not given in the results section.

5 Electrodialysis versus membrane capacitive deionisation

In the previous chapters the results of the experiments with ED and MCDI are presented. In this chapter these results are combined, outlining the differences between the two technologies in energy consumption and membrane performance. The results were validated by comparing them with results for the treatment of CTBD water with reverse osmosis.

5.1 Overall performance

Comparing the experiments, both technologies were capable of treating CTBD water. Ions were removed and no large operational problems occurred. Nonetheless there were differences in results of both experiments. Electrodialysis reached the required desalination rate, but was limited by low limiting current densities. The consequence is that a long time is needed to desalinate the water which results in a large membrane area needed. In MCDI the desalination rate was limited by the conductivity of the feed water and the maximal current that could be applied on the stack (20A). Voltea membranes gave the desired desalination, and with the PCCell membranes the conductivity of 1000µS/cm was just reached under the set conditions. However, the water recovery requirement of 66% was not met for the MCDI experiments. The desalinated water of conductivity lower than 1000µS/cm was for the Voltea membranes 62% and for PCCell membranes 40% of the total water used. Water-recovery was achieved in the ED experiment because it was operated in batch and volumes of diluate and concentrate were chosen at the start of the experiment.

5.2 Energy consumption

Energy consumptions were calculated for both systems and are presented in Figure 5-1. This graph shows the energy requirement in kWh/m^3 of both ED and MCDI for three different feed waters, all calculated based on experimental results. The first three histograms show that the energy requirement of MCDI for the treatment of CTBD water was ca. 5 times higher than treatment of the same water with ED. The difference can predominantly be attributed to the high current applied on the MCDI. The second bundle of histograms shows that the energy demand of MCDI was ca. two times higher compared to ED, for the treatment of a feed water solution of 25mmol/l NaCl with a conductivity of 3.0mS/cm. The last histograms present that the energy consumption was almost similar for both systems for the treatment of a feed water solution of 10mmol/l NaCl with a feed conductivity of 1.9mS/cm. The figure suggests that with decreasing salt concentration, energy consumption of MCDI decreases and becomes almost similar to that of ED treatment.

Two other observations which can be made from the graph are that the energy demand of ED was similar for different salt concentrations, ca. 0.4kWh/m^3. And that in MCDI, Voltea and PCCell membranes required similar energy demand for the different water types. The energy consumption of ED being on average 0.4kWh/m^3, was in line with previous research. Ortiz et. al (2005) published a paper on batch experimental work for the desalination of brackish water with electrodialysis. Energy consumption requirements calculated from experiments and model based calculations were found to be between 0.39kWh/m^{3}and 0.9kWh/m^3. Application of ED for the treatment of brine solutions of an RO plant required 7.0-8.0kWh/m^3, as shown by Korngold et. al (2009). Energy consumption of MCDI for treatment of CTBD water was 2.1kWh/m^3, which is in line with the results of Lee et.al (2006) who found an energy requirement of 1.96kWh/m^3 for the treatment of wastewater. More experimental data on the energy requirement of desalination with MCDI is outlined in Anderson et.al (2010).

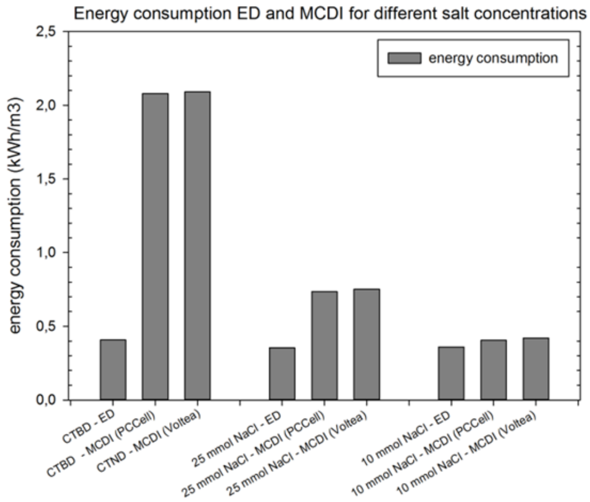


Figure 5-1 Energy demand ED and MCDI for different salt concentrations

The current efficiencies which were achieved in electrodialysis were much higher (>85%) compared to the current efficiencies obtained with MCDI (between 55% and 63%). This is an unexpected result, since MCDI claims to work at current efficiencies over 90% (Biesheuvel, 2010), compared to most frequently observed current efficiencies with ED being between 60% and 80% (Sadrzadeh, 2009). So the ED performed according to results found in literature, but MCDI gave deviating results. These low current efficiencies were partly the result of the impurity of the samples, as explained in the discussion on paragraph 4.4. In addition to this, it should be noted that the high current efficiencies found in literature, are for the desalination of light salty waters. Kim et. al (2010), for example, found current efficiencies up to 91.3% with MCDI for a NaCl solution of 200ppm. Another explanation of the low current efficiencies for MCDI can be the current applied on the system. The required current was determined with a predictive model, but seemed to be on the low side after analysing the results. However, the stack was limited to a current supply of 20A, so with the used setup, higher currents could not have been applied.

Limited literature is available on the treatment of water with a high salt concentration with MCDI. Lee et. al. (2006) is one of the few and presented in its study the possibilities of treatment of wastewater (5400µS/cm) from a thermal power plant with MCDI. The study did not show results on current efficiencies or water recoveries and it was stated that the electric energy consumption of the tested stack was 1.96kWh/m^3 for the desalination of the wastewater.

5.3 Membrane performance

5.3.1 Ion removal

Figure 5-2 presents the average ion removal of ED and MCDI during the several experiments. Ion removal was observed to be ranging from 66% up to 93%. The choice of membranes, and therefore, the applied ion exchange resin, is of influence on the removal rate and preference of certain ion. Van den Bruggen et. al (2004), stated that these properties can lead to a slower removal of divalent ions compared to monovalent ions. Difference in removal based on valence of the ion was not clearly shown in the experimental results. Furthermore, no significant difference in ion removal preferences or rates between ED and MCDI was observed. Performance of PCCell membranes application in ED and MCDI did not show a large difference. Only sulphate and potassium seemed to be removed better with the PCCell membranes in ED application compared to the MCDI application. Given these elaborations, it should be taken into account that water samples in MCDI were not pure due to the low flow rates.

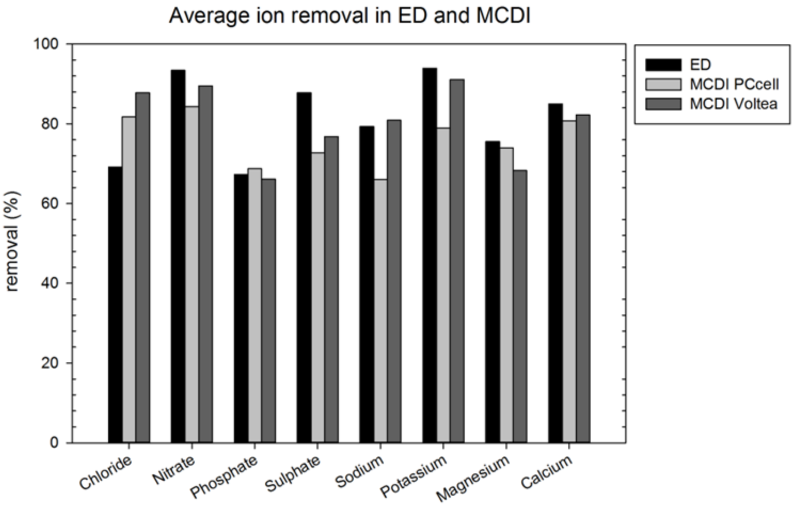


Figure 5-2 Average ion removal for ED and MCDI

5.3.2 Membrane fouling

With the inspection of the membranes, a large colour difference was clearly present between the different anion exchange membranes. The AEMs in ED seemed to have more organic fouling, as it showed to have brown deposits on the membranes. The AEM used in MCDI also showed discolouration, but not as much compared to the membranes in the ED. This distinction lays in a different applied electric field between the two setups. ED worked with high voltages (ca. 4.0V), whereas the voltage over the MCDI stack was maximally 1.5V. The velocity of particles moving towards the electrode when an electric field is applied is known as the electrophoretic mobility. This velocity is influenced by several factors such as the strength of the field, the viscosity and the dielectric constant of the medium and the zeta potential (Anderson, 2010). Zeta potentials of organic foulants have a highly negatively charge, which implies that they can easily be adsorbed on the surface of a positively charged anion exchange membrane, resulting in fouling on the membrane (Lee, 2009). However, it should be noticed, that unless the difference in applied electric field, deterioration of the membranes, in terms of permselectivity and resistance, was limited as shown in Table 4-4.

5.4 Comparison with reverse osmosis

Given the discussion above, it can be stated that, in terms of energy consumption, it is more interesting to desalinate CTBD water with electrodialysis than with membrane capacitive deionization. The results on energy consumption with ED and MCDI presented in the previous paragraph, showed that the technologies become competitive at a salt concentration of ca. 10mmol/l. But how does this energy consumption and the overall performance relate to the treatment of CTBD water with reverse osmosis? RO is a membrane separation technology which has proven its maturity over the past decades. Numerous of RO plants have been build and there is much experience gained on the operation of such a system under different conditions (Greenlee, 2009). According to Strathmann (2004), the main advantages of electrodialysis compared to reverse osmosis are:

- High water recovery rates, even for raw water with high sulphate content;
- Long useful life of membranes due to higher chemical and mechanical stability;
- Operation at elevated temperatures up to 50°C possible;
- Less membrane fouling or scaling due to process reversal;
- Less raw water treatment;
- Ion exchange membranes tolerate higher level of chlorine (up to 1ppm) and extreme pH values;
- The process can easily be adjusted to varying feed water quality;
- Easy start-up and shut down for intermitted operation.

Besides the advantages, there are also some disadvantages. RO produces highly purified water that is free of particles and neutral compounds like viruses and bacteria. Electrodialysis is a technology that only removes charged compounds and hence, neutral compounds are not removed. For the desalination of CTBD water and its reuse as process water, disinfection of the water stream is not required. This makes ED(R) an interesting technology to mildly desalinate CTBD water.

Considering the costs, electrodialysis and reverse osmosis are competitive at a certain feed water salt concentration. Figure 5-3 shows the relative water production costs for reverse osmosis, distillation, electrodialysis and ion exchange as a function of the salt concentration. The figure shows that from around 7.5g/l salts and higher, the relative water production costs become lower for RO than for ED. The total amount of salts in CTBD water of the Dow chemical plant is 2.7g/l, which suggests that ED treatment is economically more interesting compared to RO.

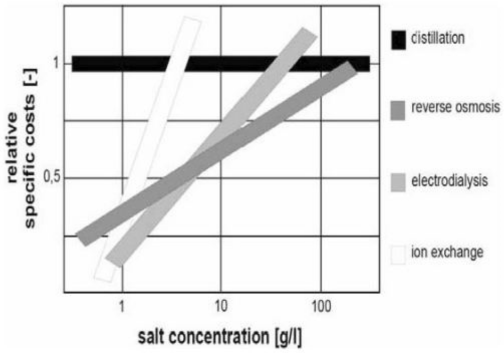


Figure 5-3 Relative water production cost of different desalination technologies, as a function of the salt concentration. (Fritzmann, 2007)

6 Electrodialysis pilot design

The discussion in Chapter 5 showed that, electrodialysis is a more energy efficient system to desalinate cooling tower blowdown water compared to membrane capacitive deionization. It is therefore chosen to further study the treatment of CTBD water with electrodialysis. In this chapter a design is proposed for an EDR pilot installation with a desalination capacity of 4m^3/h. Starting point for the design was a pilot application which resembles a full scale electrodialysis reversal plant. This resulted in a continuous EDR system with multiple stacks so that the system can be operated with high velocities. Focus in this design was on the EDR stacks and therefore a simple pre-treatment system was chosen. In a real application further research is required to determine a proper pre-treatment configuration. The calculations which have been made for the design of the EDR stack and presented in Appendix D. In this chapter, the design consideration and operational aspects of the pilot are discussed.

6.1 Proposed design

Figure 6-1 presents the process flow diagram of the proposed pilot design. A larger plot of the figure is given in Appendix D. In the pilot there are two main processes; first of all there is the pre-treatment which is designed as a cartridge filter process. Secondly there is the electrodialysis unit itself, which consists of four stages. It was chosen to applied electrodialysis reversal (EDR) which provides the opportunity of the reversal of polarity of the system. The water needs to pass all stacks to achieve the desired desalination rate. Besides the two processes is there a facility for chemical cleaning of, and chemical dosing to the system. There are two main water streams in electrodialysis reversal: the diluate and the concentrate stream. It is assumed that the produced clean water and waste stream are discharged by the sewer. All aspects of the design are now discussed in more detail.

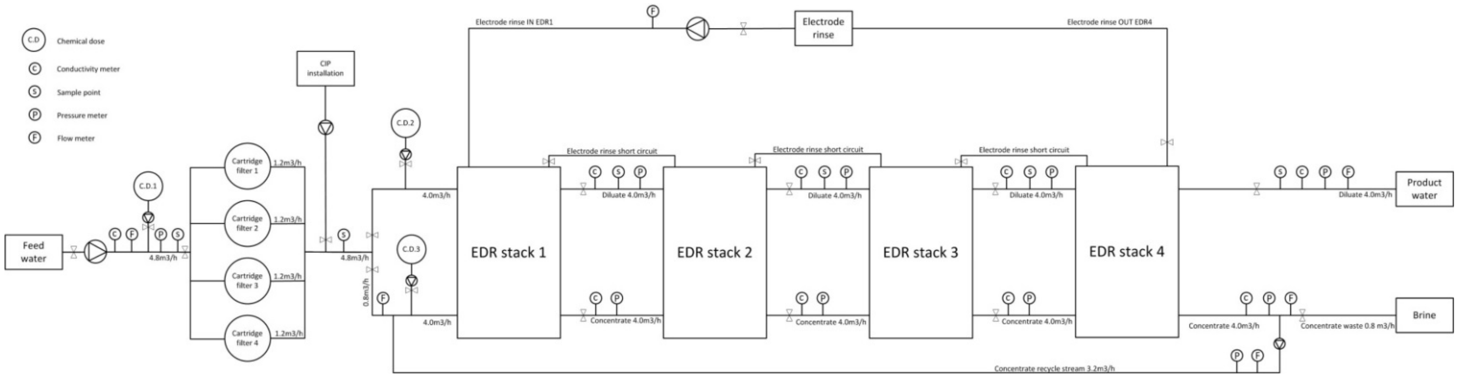


Figure 6-1 Process and flow diagram of the EDR pilot

6.1.1 Pre-treatment

Electrodialysis reversal requires minimal pre-treatment; particles larger than 10µm should be removed (Lenntech) and feed water concentrations for iron and manganese must be kept below 0.3mg/l and 0.05mg/l (Strathmann, 2010). A set of cartridge filters are often applied in practice as a pre-treatment for electrodialysis reversal. Aim is to remove large particles, and it might be beneficial to remove some of the organic content in the water to reduce the possibilities of membrane fouling. In the proposed design four cartridge filters are installed after the point where the feed water enters the pilot hall and they can each filter 1.2m^3/h. These filters are easy to install and can be cleaned or replaced when they are clogged. Cartridge filters can have different pore sizes; a 10µm filter was used in the experimental work and can also suffice in the pilot design.

6.1.2 Electrodialysis stack

After pre-filtration the water flows into the electrodialysis reversal stacks. The four stacks each hold 67 cell pairs and water flows with a velocity of 0.048m/s through each stack. All the cell pairs have the same dimensions and one membrane has an area of 0.5*0.5m. The operating current density is for the EDR stacks below the limiting current density of the incoming water, to prevent an increase in voltage due to water splitting. The operated current densities and the limiting current densities of the water leaving each stack are given in Table 6-1. The total desalinated water production is 4m^3/h. It should be noticed that the stacks operate at a current density far below the LCD. The calculations were made for desalination of NaCl solutions. In practice, CTBD water that has a lower limiting current density flows through the stacks. Hence, a margin is created in the design to account for this difference. In the stack there are two main water streams which should be considered carefully in the design process of an EDR unit: the diluate and the concentrate. The third stream, the electrode rinse is chosen as a 0.25M Na_2SO_4 solution and is recirculated over the four stacks. The volume of this solution is generally chosen as the production rate of the product water, which is in this case 4m^3.

Table 6-1 Salt removal and current densities of the 4 EDR stacks

	NaCl eq. removal (mmol/l)	**Salt removal (mmol/s)**	**Operating CD (A/m^2)**	**LCD (A/m^2)**
Stack 1	9.6	0.096	61.8	107.0
Stack 2	6.6	0.066	42.5	69.7
Stack 3	3.6	0.036	23.2	44.8
Stack 4	0.6	0.006	3.9	2.3

Diluate stream

The first steam is the diluate which is pre-filtered CTBD water that is introduced in the EDR stack. After the passage of the first stack, the diluate has a conductivity of ca. 2800µS/cm, and successively flows into the second EDR stack. This stack operates at a lower current density compared to the first stack, and removes salt from the water so that the product water quality is ca. 1900µS/cm. The water has a conductivity of ca. 1300µS/cm after passage along the third stack. The water reaches the required product water conductivity of 1000µS/cm after passing the last EDR stack.

Electrodialysis reversal only removes charged particles; the product water is therefore not disinfected and can hold for example bacteria and viruses. Whether post-treatment of the desalinated water is needed, depends on the required product water quality which is in this case cooling tower makeup water (water qualities given in Table 2-1). Additional treatment might be needed for the removal of TOC. On the other hand, removal of TOC in the pre-treatment might be of preference on the operation of the electrodialysis, meaning that there is less fouling potential.

Concentrate stream

The second stream is the concentrate stream which has as its source pre-treated cooling tower blow. In some cases in might be beneficial to not use the feed water source for the concentrate, because it can introduce extra substances which enhance the possibility of fouling and scaling. One can then choose for artificial water like a NaCl solution. Recycling of the concentrate stream establishes the water recovery. If there would be no recirculation of the concentrate stream, and flows for diluate and concentrate are similar, a water recovery of 50% is achieved. Other factors which contribute to the water recovery are membrane cleaning by reversing of the polarity and the volume of the electrode rinse solution. In this pilot design a water recovery of about 80% is established by recycling 3.2m^3/h of the concentrate stream. This means that fresh concentrate feed is introduced at a flow rate of 0.8m^3/h and mixed (inline) with the recycled water. Recycling of the concentrate can be over the four stacks or per individual stack. The process flow diagram shows recycling over the four stacks. It can be considered in the pilot study to operate the EDR stack in a counter current flow. This means that the concentrate stream is introduced at the end of the second stack, and the outcome is at the front side of the first EDR stack. In this way, salt concentrations in the concentrate in the last (fourth) EDR stack are lower than in the first EDR stack. This operation in counter current involves that scaling in the concentrate side is likely to happen in the first stack. In co-current operation will precipitation of salts occur in the last stack. Experiments with the pilot should show whether scaling occurs due to recycling and if higher water recoveries can be achieved.

6.1.3 Chemical requirement and cleaning

Chemicals might need to be added to improve the operation of the system. A pilot installation is the ideal way to test which and in what concentrations chemical should be dosed. One can think of dosing chlorine to the diluate stream to decrease the fouling potential of the water. This is given in the process and flow diagram by chemical dose point 2. EDR can operate on water with a chlorine concentration up to 0.5mg/l to control the biological nature of the feed water (Valero, 2011). Antiscalant is regularly dosed to the concentrate stream (chemical dose point 3 in the process and flow diagram) to control the risk of scaling and to increase the water recovery (Allison, 1993).

An acid wash of the membranes can be applied in case scaling does occur on the membranes. Biofouling is removed from anion exchange membranes by an alkaline cleaning. In the situation of membrane cleaning for both scaling and fouling, acid cleaning should be carried out before alkaline cleaning. Chemical cleaning in the proposed pilot design is operated by the chemical cleaning in place installation (CIP). During a chemical cleaning, the normal operation of the EDR unit is stopped and are chemicals pumped through the EDR stacks by the CIP installation.

Besides these chemical cleanings provides electrodialysis reversal an additional treatment possibility. By reversing the polarity the system, all charged particles are released from the membrane and removed in a waste stream. EDR removes foulants on the membranes significantly and restores the capacity of the system (Korngold, 1970). The frequency of polarity change and chemical cleaning depends on the feed water quality and should be tested in the pilot.

Both cleaning methods produce an extra waste stream of 2%-5%. The waste stream created by reversing the polarity is discharged in the same piping as in desalination operation of the EDR. In full scale application extra piping and valves separate the waste stream from the product water. Furthermore, waste treatment should be considered in a full scale application. The quality of the brine might be of good quality to be reused for another process. With the dosing of chemicals for either operational or cleaning purposes, should it be taken into account that ion selective membranes can be damage when concentrations are too high (Valero, 2011).

6.1.4 Operation and control

The pilot requires a couple of pumps to deliver the flows and are given in the process and flow diagram. A control panel is installed to operate the EDR stacks and the pumps. In this panel flows, conductivities, pressure etc. are monitored online. Conductivity meters are placed at several points in the process and sample points are installed at the feed intake and after each EDR stack to be able to take water samples for analysis. Furthermore, there are several flow meters and pressure meters installed to record these parameters.

Flexibility

This design is made for the desalination of cooling tower blowdown water. Yet, Dow has more (industrial) waste streams which they want to reuse. These water streams can also be tested in the pilot study. The rain water runoff from the spuikom is not a continuous water stream and it might therefore be an option to blend this was together with the other water sources in certain periods. The blending and the effects of longer term on the systems should be tested in the pilot.

The fact that the pilot has four EDR stacks enlarges the flexibility of testing the system. As said before, the concentrate stream can be operated co- or counter-current. Moreover, tests are possible with less than four stacks, in for example the desalination of sweet WWTP effluent. This water is less salty and therefore requires a shorter contact time or lower current on the stacks. Having a four stage EDR pilot also gives the possibility to test different membranes at the same time. The pilot design is made for one street, for full scale application, more streets might be required to increase the redundancy of the system. Buffer tanks should be incorporated for a larger scale design to control fluctuations at the intake and in the process. More suggestions for the pilot study are given in the recommendation section.

6.2 Energy consumption

There are two main components which contribute to the energy consumption in desalination with electrodialysis: 1) energy required for the operation of the direct current to introduce a constant current over the stacks, 2) energy to pump the water through the stacks and pipes. The first requirement is determined by the required desalination rate, feed water quality and membrane use. Energy consumption for water transport is determined by the pressure losses over the filtration and EDR stacks and the resistance in the pipes.

6.2.1 Staging in Electrodialysis

In the pilot design, four EDR stacks are placed after each other which is needed to reach the required salt removal. Staging of the process can also have a positive effect on the energy consumption. To determine the order of magnitude for the benefit of staging, some additional experiments were carried out. A description of this experiment is presented in Appendix E and the main outcome is shown in Figure 6-3. This graph shows the energy requirement for 4 different experiments. The first bar presents the staging experiment. In this experiment, the constant current was introduced on the system and was lowered in 3 steps at different conductivities from 0.4A to 0.2A down to 0.1A. The other 3 bars show the energy requirement when the experiment would be carried out with a constant current of 0.4A, 0.2A or 0.1A. The graph shows that by applying stages, the energy consumption decreased. It should be taken into account that the figures for the constant current operation (0.4, 0.2, and 0.1) are extrapolated from the graph of the staged experiment. The actual demand might therefore be a slightly different. Moreover, it should be bared in mind that when the electrodialysis is operated with a constant current of 0.4A or 0.2A, the limiting current density is exceeded. A constant current of 0.1A is below the LCD of the desalinated water, and therefore gives a good comparison. It can be concluded from the graph that applying different stages is about three times more energy efficient compared to the desalination with a constant current of 0.1A, which is below the limiting current density of the end water product quality.

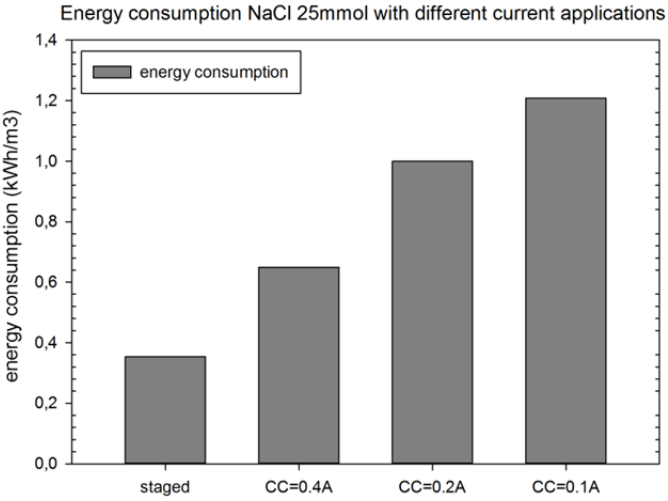


Figure 6-3 Energy requirement for 25mmol/l NaCl desalination with different current applications

6.3 Cost of an EDR plant

The costs of a process are of importance in the selection of a certain technology and the construction of a plant. Total costs are divided in investment costs and operational costs. The investment costs of an electrodialysis reversal plant are the costs for all the required equipment, in which the EDR stacks plus the membranes are of great importance. Costs of other items such as pumps, pre-treatment, monitoring equipment, piping and control devices are also accounted for in the investment costs and are independent of the feed water solution. The required membrane area is of main influence on the investment costs. The area needed is determined by the feed, diluate and concentrate water quality and the required production rate. Membrane lifetime should be taken into account, and is also strongly dependent on the feed water quality and operational conditions. The average membrane lifetime is experienced to be 5 up to 7 years. The lifetime of the power supply, pumps, piping etc., is on average 10 up to 20 years (Strathmann, 2004). Total investment costs are difficult to estimate since membrane and other equipment costs vary widely depending on the manufacturer, plant size and location.

Operational costs are determined by labour, maintenance and energy. The first to factors are proportional to the size of the plant and often described as a fraction of the investment costs. The operational costs related to energy consumption are composed of the following factors:

- Energy requirement for the actual desalting process;
- Energy consumption by pumps to transport the water through the process and for the operation of process control devices.

The energy requirement for the electrode reactions, regarding the desalting process, can be neglected because of a large amount of cells (>200) between the electrodes. The energy demand for the process itself depends strongly on the feed water quality, required amount of desalination and the membrane use. Costs are increasing with the feed water salinity assuming a similar product water quality. From the experimental work, an energy demand of ca. 0.4kWh/m^3 was derived. Having a plant with a capacity of 4m^3 and costs for energy being 0.07€/kWh, results in 0.112€/h for the energy costs contributed by the desalting process. Figure 6-4 illustrates the electrodialysis desalination costs as a function of the feed water quality assuming a constant product concentration.

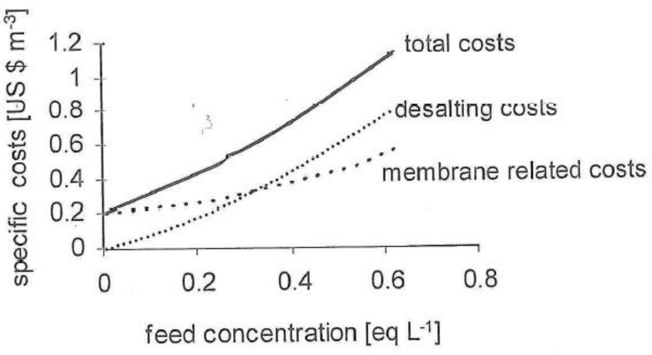


Figure 6-4 Electrodialysis desalination costs as a function of the feed solution concentration (Strathmann, 2004)

7 Conclusions & recommendations

In the last chapter of this report, conclusions regarding the research are drawn and recommendations are presented for further research.

7.1 Conclusions

In this research it was investigated whether electrodialysis and membrane capacitive deionization are suitable for the desalination of cooling tower blowdown water. This CTBD water is a challenging water source to treat because it contains high concentrations of salts (predominately Ca^{2+}, Na^+, SO_4^{2-} and Cl^-) and other additives like antiscalants and corrosion inhibitors. The main requirement for the desalination of cooling tower blowdown water was that the product water quality should have a conductivity of 1000µS/cm or lower. The study showed that electrodialysis and membrane capacitive deionization, are both capable of treating cooling tower blowdown water. However there are differences in operation between the two technologies.

The process of electrodialysis is limited by the limiting current density of the feed water. The limiting current density depends on the salt concentration of the feed water, the flow rate in the cells and the membrane type. In this study it was found that the LCD increases with increasing salt concentration and flow rate in the cell, which is in accordance with previous studies on the limiting current density (Lee, 2006). The limiting current density of the cooling tower blowdown water was experimentally determined for different dilutions. The raw CTBD water had a LCD of $56.3A/m^2$ and an 8x diluted CTBD water, which equals an end conductivity of 1000µS/cm, had a LCD of $23.43A/m^2$. Experiments with different model water with varying salt concentrations showed that the LCD is of the CTBD water was mainly determined by the presence of calcium, sodium, chloride and magnesium ions.

Desalination of CTBD water with membrane capacitive deionization was mainly limited by the conductivity of the feed water and the maximal current that could be applied on the stack (20A). Two membrane types were tested in the MCDI experiment, Voltea membranes and PCCell membranes. Both stacks showed that the required desalination rate could be achieved; however, the water recovery requirement of 66% was not met during the experiments. The desalinated water of conductivity lower than 1000µS/cm was for Voltea membranes 62%, and for PCCell membranes 40% of the total water used.

When comparing the membrane performance of both systems, no striking results were observed. Similar ion removal rates were observed and no clear differences in ion selectivity was obtained. Due to the short time period of the experiments, nothing substantial can be concluded on the membrane fouling and scaling of the system. Membrane degradation was determined based on permselectivity and resistance. The results show that the AEMs degrade more than the CEMs, for both ED and MCDI. Even though nothing significant related to fouling can be said in comparison of the two systems, some TOC fouling was observed on the AEMs in the ED stack. In these experiments, TOC fouling on the membranes was observed during the first couple of runs, where after it stabilizes to no removal of TOC in the successive runs. In relation to this, the ion removal rate seemed to be constant during all runs. Thus, TOC fouling of the membranes does not seem to have an influence on the ion removal efficiency in electrodialysis.

Main difference in the desalination of cooling tower blowdown water with ED and MCDI lays in the energy requirement. The energy needed for MCDI was 5 times higher ($2.1kWh/m^3$) compared to ED (0.4kWh/m3). This large difference makes that it is more interesting to desalinate the water using electrodialysis. Experimental results with different salt concentrations showed that with decreasing salt concentration, the energy demand of MCDI also decreased, whereas the energy demand of ED remained constant. The energy demand of ED and MCDI were found to be similar for the treatment of a 10mmol/l NaCl solution. The observation that the energy demand remained constant with varying salt concentrations entails that ED is most likely also energy efficient for the treatment of the other three water streams at Dow, spuikom and sweet waste water effluent.

In conclusion can be said that electrodialysis is a more convenient technology for the desalination of cooling tower blowdown water compared to membrane capacitive deionization. This difference lays mainly in the energy consumption of both technologies. This study did not show any significant results on operational problems like membrane fouling and scaling. Besides, experiments conducted in this thesis were all short term; therefore nothing can be said about the longer term operation of a system. Electrodialysis is a technology which is comparative with reverse osmosis for certain feed water salt concentrations.

Further research can be conducted in a pilot study which is a common step before constructing a new technology on larger scale. This thesis proposed a pilot installation for electrodialysis reversal consisting of pre-treatment with cartridge filters and a four stage electrodialysis configuration with each stack holding 67 cell pairs. It is a robust design which can be used to research all kind of aspects of the process, and resembles a full scale configuration.

7.2 Recommendations

Recommendations for further research are made based on the experimental results and the discussion. The general conclusion of this thesis is that electrodialysis is more energy efficient for the treatment of cooling tower blowdown water compared to membrane capacitive deionization. In addition to this, it was decided in the E4Water Dow case to start a pilot test with EDR. Therefore, the recommendations given in this section have a focus, on further research of desalination with electrodialysis in a pilot study. Membrane capacitive deionization might be interesting for the treatment of the less salty waters of Dow, but these are not considered here.

- The proposed pilot design should be optimized in terms of pump performance, piping and monitoring;
- Further research on the operation of electrodialysis is needed. In this work, no investigation was done on the reversal of the polarity and its influence on the performance. It is adviced to research the efficiency and frequency of reversing polarity;
- The optimal operation conditions regarding current and flow, should be tested in the pilot study;
- Longer testing is advised to gain insight in the long term performance of the system;
- Cleaning procedures of the membranes and spacers should be studied in more detail, to determine the frequency of cleaning and the chemical requirement;
- Dosage of antiscalant (in the concentrate) and chlorine (in the diluate) must be tested for its effect on the fouling and scaling potential of the system;
- It is advised to test different kind of ion selective membranes in the application of EDR. A ion selective membrane which is more permeable for sulphate and calcium, which are present in high concentrations in the CTBD water, might enhance the performance of the system;

- It is advised to conduct experiments to investigate the performance of the concentrate flow. One can think of researching the effect of counter current operation of the concentrate stream, or recirculation of the concentrate stream per stack, instead of over the four stacks;
- This thesis suggested a sodium sulphate solution for the electrode rinse. It might be of positive influence on the process to use another rinse solution. Therefore it is suggested to test different type of electrode rinse solutions and concentrations;
- The other water sources available from Dow should be tested in the pilot study. Because the salt concentration in these waters are lower than CTBD water, it is expected that these water can easily be desalinated with EDR;
- Based on longer term testing and insight in frequency of cleaning, more accurate calculations can be made regarding the energy consumption;
- It is recommended to determine the water quality of the waste streams which are produced in EDR. Further treatment and reuse of these concentrated waste streams can be of interest;
- Conducting a pilot study will also gain more specific information on investment and operational costs.

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9 Appendices

Appendix A: Factsheets desalination technologies

Appendix B: Limiting current density graphs for different salts, concentrations and flow rates

Appendix C: Membrane cleaning procedure of electrodialysis membranes

Appendix D: Calculations of electrodialysis pilot design

Appendix E: Electrodialysis experiment with staging of the constant current

Appendix A.

Category	Name	Sub criteria/ Notes		Reference
Technology	**Name**	**name and abbreviation of the technology**		
	Description	short description of technology		
	Status	lab/demo/full scale		
	Most common applications	In which industry (drinking water/ industrial water/ waste water) and which purpose (desalination/softening/disinfection etc.)		
Water quality	**Influent quality requirement**	***pre-treatment needed***	indicates what should be removed in pre-treatment (if possible in concentrations)	
		type of pre-treatment	indicates what kind of pre-treatment is needed	
		limiting factors	indication of limiting factors such as fouling/scaling/pressure/availability of heat and other processes	
		salinity range TDS	min and max salinity range which the system can cope with, and for which salinity's is it generally applied	
		fouling extent	explains kind of expected fouling: organic biofouling, inorganic etc.	
	Effluent quality possibilities	***rejection of monovalent ions***	figure expressed in %	
		rejection of divalent ions	figure expressed in %	
		rejection of organics	figure expressed in %	
		rejections of colloids	figure expressed in %	
		biological stability	presence of bacteria etc. in the effluent	
		water quality	Effluent water quality, salinity concentration expressed in mg TDS /l	
	Waste streams	***discharge problems***	indicate whether the brine needs to be treated before discharge	
		water quality	indicated how concentrated the waste stream is and if is contains a lot of chemicals	
		valuables recovery possible	indicated if heat or nutrients can be recovered from the waste stream	
Process parameters	**Water recovery**	recovery possibilities with the technique, in case of brackish water desalination		
	Capacity limits	at which capacity the technology is most (cost) efficient: small: 1-100 m^3/d - medium: 100-1.000 m^3/d - large: >1,000 m^3/d		
	Flexibility in operation	whether the effluent water quality can be influenced during operation (tuneable)		
	Fouling control	what can be done/ which measures need to be taken, to prevent/control fouling		
	Cleaning of the system	how the system can be cleaned periodically		
	Space requirements	area needed for the installation (m2/m^3)		
	Life span of the system	expected lifetime of the system, in case of membrane systems the membrane life time		
Costs	**Capital costs**	costs per m^3 produced water with a depreciation of 10 years. Indication of what the costs include: installation, piping & equipment, pre-treatment, post-treatment, building etc.		
	Operational costs	***energy requirement***	expressed in kWh/m^3 (with indication of reference salinity and temperature)	
		chemical requirement	only if chemicals are determining in the process, a figure is given.	
Further information	**Main suppliers**			
	Reference projects			
	Research needs			
	Recommended literature			

Category	Name	Sub criteria/ Notes		Reference
Technology	Name	**Reverse Osmosis (RO)**		
	Description	RO is a pressure driven membrane process in which water is filtered through a membrane with pores of <0.001µm. Driving force: pressure		
	Status	full scale		
	Most common applications	seawater and brackish water desalination, drinking water treatment and industry		
Water quality	Influent quality requirement	***pre-treatment needed***	yes, to remove organic, colloidal and biological matter that can cause fouling	*The Nalco waterhandbook*
		type of pre-treatment	coagulation, flocculation, sedimentation, filtration, UF	
		limiting factors	formation of solid compounds and driving pressure	
		salinity range TDS	100-25,000 mg/l for BWRO, can go up to 50,000 for SWRO	*Water desalting, planning guide for water utilities, AWWA*
		fouling extent	fouling and scaling can be a problem and should be controlled	
	Effluent quality possibilities	***rejection of monovalent ions***	can be up to 99,9(9)%	*The Nalco waterhandbook*
		rejection of divalent ions	can be up to 99,9(9)%	*The Nalco waterhandbook*
		rejection of organics	can be up to 99,9(9)%	*Water desalting, planning guide for water utilities, AWWA*
		rejections of colloids	100%	
		biological stability	effluent is biological stable (viruses and bacteria are removed)	
		water quality	pure, disinfected water; TDS , <100 mg/L	*State of the art of RO desalination, Fritzmann et al. 2006*
	Waste streams	***discharge problems***	concentrate might need treatment before discharge	
		water quality	high concentrated stream, can contain chemicals (anti-scalant) if added	
		valuables recovery possible	energy recirculation possible	
Process parameters	Water recovery	60-85% for brackish water desalination, sea water desalination can be up to 50%		*Water desalting, planning guide for water utilities, AWWA*
	Capacity limits	can be cost effective for all ranges of plant capacity (small, medium and large)		
	Flexibility in operation	staging can be applied to increase flexibility and improve salt removal, stable influent quality from pre-treatment is desirable. Process is not tuneable, partial desalination can be done by applying a by-pass		
	Fouling control	dosing of anti-scalants or chemical cleaning		
	Cleaning of the system	chemical cleaning (in place)		
	Space requirements	depends on feed water and required effluent quality. In general compact system due to high specific area of the spiral membranes. Indication for plant with capacity of 37,850m^3/day = 4000m^2 for BWRO (influent salinity unknown)		*Water desalting, planning guide for water utilities, AWWA*
	Life span of the system	depends on feed water and operational parameters, membrane lifespan: 3-7 years		
Costs	Capital costs	brackish water desalination (2,000 - 10,000 ppm), plant capacity (5,000-60,000 m^3/d), costs: 0,21-0,43 euro ct/m^3 (not indicated what costs include)		*water desalination cost literature: review and assessment, Ioannis (2007)*
	Operational costs	***energy requirement***	directly related to the salt concentration, 0,4-7 kWh/m^3 (depends on energy recovery)	*State of the art of RO desalination, Fritzmann et al. 2006*
		chemical requirement	3,18 euro ct/m^3 for pre-treatment, conditioning, membrane cleaning, post-treatment (ref. capacity 140,000m^3/d)	*State of the art of RO desalination, Fritzmann et al. 2006*
Further information	Main suppliers	Numerous		
	Reference projects	Numerous		
	Research needs			
	Recommended literature	a lot of literature available on RO research, see also references		

Category	Name	Sub criteria/ Notes		Reference
Technology	**Name**	**Nano Filtration (NF)**		
	Description	NF is a pressure driven membrane process in which water is filtered through a membrane with pores of <0.01µm. Driving force: pressure		
	Status	full scale		
	Most common applications	brackish water desalination, drinking water treatment (softening), pre-treatment for RO and industry		
Water quality	**Influent quality requirement**	***pre-treatment needed***	yes, to remove organic, colloidal and biological matter that can cause fouling	
		type of pre-treatment	coagulation, flocculation, sedimentation, filtration, UF	
		limiting factors	formation of solid compounds and driving pressure	
		salinity range TDS	500-25,000 mg/l	*Technical assessment of produced water treatment technologies, 2009*
		fouling extent	fouling and scaling can be a problem and should be controlled	
	Effluent quality possibilities	***rejection of monovalent ions***	50-95%	*The Nalco waterhandbook*
		rejection of divalent ions	90-98%	*The Nalco waterhandbook*
		rejection of organics	removal of large organics	
		rejections of colloids	100%	
		biological stability	effluent is biological stable	
		water quality	pure, disinfected water, TDS <100 mg/L	*State of the art of RO desalination, Fritzmann et al. 2006*
	Waste streams	***discharge problems***	large recovery, so small volume of concentrated stream, treatment might be needed	
		water quality	concentrated stream, can contain chemicals (anti-scalant) if added	
		valuables recovery possible	energy recirculation possible	
Process parameters	**Water recovery**	70-90% for brackish water desalination		*Technical assessment of produced water treatment technologies, 2009*
	Capacity limits	can be cost effective for all ranges of plant capacity (small, medium and large)		
	Flexibility in operation	staging can be applied to increase flexibility and improve salt removal, stable influent quality from pre-treatment is desirable. Process is not tuneable, partial desalination can be done by applying a by-pass		
	Fouling control	dosing of scale inhibitor and caustic can be used to prevent scaling or fouling		*Technical assessment of produced water treatment technologies, 2009*
	Cleaning of the system	chemical cleaning (in place)		
	Space requirements	depends on feed water and required effluent quality. In general compact system due to high specific area of the spiral membranes		
	Life span of the system	depends on operating conditions, membrane replacement after 3-7 years		
Costs	**Capital costs**	0,25 euro/m^3 (for 100,000m^3/d, treatment of surface water)		*Performance and cost estimation of nanofiltration for surface water treatment in drinkin*
	Operational costs	***energy requirement***	directly related to the salt concentration, 0,4-7 kWh/m^3 (depends on energy recovery)	*State of the art of RO desalination, Fritzmann et al. 2006*
		chemical requirement		
Further information	**Main suppliers**	Numerous		
	Reference projects	Numerous		
	Research needs			
	Recommended literature	a lot of literature available on NF research, see also references		

Category	Name	Sub criteria/ Notes		Reference
Technology	**Name**	**Electrodialysis (ED)**		
	Description	ED is an electrochemical process for the separation of ions across charged membranes from one solution to another under the influence of an electrical potential difference as a driving force. EDR (electrodialysis reversal) is based on the same principle, however, electrode polarity is periodically reversed to facilitate cleaning of the ED membrane. Driving force: potential applied between 2 electrodes		
	Status	full scale		
	Most common applications	main application is desalination of brackish water for domestic and industrial use		
Water quality	**Influent quality requirement**	***pre-treatment needed***	removal of suspended solids (<10µm) and substances that are able to neutralize the membrane (large organic anions, colloids, iron (0,3 mg/l and maganese 0,05 mg/l oxides)	
		type of pre-treatment	filtration, optional: flocculation and activated carbon	
		limiting factors	fouling/scaling, current efficiency, osmosis, diffusion, counter effects of co-ion transport	
		salinity range TDS	500-8,000 mg/l	*Electrodialysis, a mature technology with miltitude of new applications 2010, H. Strathmann*
		fouling extent	predominantly deposit of negatively charged colloids on anion membrane	*Surface and wastewater desalination by EDR, R.P. Allison (2008)*
	Effluent quality possibilities	***rejection of monovalent ions***	50-90%	*Water desalting, planning guide for water utilities, AWWA*
		rejection of divalent ions	50-90%	*Water desalting, planning guide for water utilities, AWWA*
		rejection of organics	no, organics generally pass through the ED process	*Water desalting, planning guide for water utilities, AWWA*
		rejections of colloids	> 90%	
		biological stability	ED is not a barrier for microorganisms	
		water quality	not disinfected (uncharged components are not removed), TDS 10 - 8000 mg/l (strongly depended on influent quality and applied voltage)	*State of the art of RO desalination, Fritzmann et al. 2006*
	Waste streams	***discharge problems***	concentrate might need treatment before disposal	
		water quality	concentrated stream , does not contain a lot of chemicals	
		valuables recovery possible	salt can be recovered, concentrate can be recycled to increase recovery	
Process parameters	**Water recovery**	70-95%, for brackish water desalination		
	Capacity limits	can be cost effective for all ranges of plant capacity, most applications known with small and medium plants		
	Flexibility in operation	fairly flexible for varying influent water quality, robust. Staging can be applied to create more flexibility and increase salt removal. System is tuneable as the electrical potential can be regulated.		*Technical assessment of produced water treatment technologies, 2009*
	Fouling control	scale inhibitor and acid can be dosed to prevent scaling		
	Cleaning of the system	clean in place by reversal of the polarity of the applied electrical potential to remove precipitated colloids and salts (EDR). Chemical cleaning can also be applied		
	Space requirements	depends on feed water and required effluent quality. Indication for plant with capacity of 37,850m^3/day = 4000m^2 (influent salinity unknown)		*Water desalting, planning guide for water utilities, AWWA*
	Life span of the system	membrane: 5-10 years		
Costs	**Capital costs**	0,13 euro/m^3 for treatment of 1,000-2,000 mg TDS/l, treatment of 1300m^3/d		*Technical assessment of produced water treatment technologies, 2009*
	Operational costs	***energy requirement***	0,14-0,20 kWh/m^3	*Technical assessment of produced water treatment technologies, 2009*
		chemical requirement	only used for process control and periodic cleaning	
Further information	**Main suppliers**	numerous		
	Reference projects	numerous		
	Research needs			
	Recommended literature	a lot of literature available on ED research, see also references		

Category	Name	Sub criteria/ Notes		Reference
Technology	**Name**	**Memstill**		
	Description	Membrane distillation: desalination by evaporation of water through hydrophobic membranes based on difference in vapour pressure at different temperature		
	Status	demo		
	Most common applications	main application is desalination of brackisch water for domestic and industrial use		
Water quality	**Influent quality requirement**	***pre-treatment needed***	very little, suspended solids removal needed, surfactants removal is needed	
		type of pre-treatment	sand filtration	
		limiting factors	volatile organics are not rejected. Surfactants and some other organic components may cause leakage of the membrane	
		salinity range TDS (mg/L)	up to precipitation point	
		fouling extend	because of high hydrophobicity of membranes is fouling not a problem. Influent with high TOC is allowed	
		fouling control	not actively needed because of high operational temperature	
	Effluent quality possibilities	***rejection of monovalent ions***	100%	
		rejection of divalent ions	100%	
		rejection of organics	depends on volatility	
		rejections of colloids	100%	
		biological stability	good stability because of high temperature (higher than 60C)	
		water quality	distilled water	
		Tuneable: partial desal possible?	total desalination, concentration of feed flow possible to precipitation point, depending on stream, up to 95%	
	Waste streams	***discharge problems***	concentrate	
		water quality	heat treated	
		valuables recovery possible	If concentrate can be crystallized	
Process parameters	**Water recovery**	up to 95%		
	Capacity limits			
	Flexibility in operation			
	Fouling control	cleaning in place possible		
	Cleaning of the system			
	Space requirements			
	Life span of the system			
Costs	**Capital costs**	Investment costs (€/m3/yr)	Zie tabel hieronder	
	Operational costs	***energy requirement***	Zie tabel hieronder	
		chemical requirement	chemicals only needed for cleaning	
Further information	**Main suppliers**	(membrane units for) pilots are supplied by Aquastill		
	Reference projects			
	Research needs	• Maximum achievable recovery based on composition (salt composition and concentration) • Quality of product water (conductivity) • Membrane behavior based on composition (effect of organic compounds on membrane performance) • Energy consumption and energy costs		
	Recommended literature	J. Hanemaaijer et al.; Memstill membrane destillation: A near-future technology for sea water desalination; Memstill info 30-05-2007; 2007		

Category	Name	Sub criteria/ Notes		Reference
Technology	Name	**Multi Stage Flash Distillation (MSF)**		
	Description	MSF distillation is a process in which pre-heated (115°C)water is lead into a stage with lower pressure where the water immediately boils or flashes into steam. Generally the process consists of several stages. Driving force: heat		
	Status	full scale		
	Most common applications	desalination of brackish and sea water, especially in warm areas like the middle east. Often combined with power generation		
Water quality	Influent quality requirement	***pre-treatment needed***	yes, but only to remove large particles	
		type of pre-treatment	sand filtration, coagulation, sedimentation	
		limiting factors	availability of heat	
		salinity range TDS	8,000-50,000 mg/l	*Water desalting, planning guide for water utilities, AWWA*
		fouling extent	major problem is scaling in heat transfer surfaces	
	Effluent quality possibilities	***rejection of monovalent ions***	>99%	
		rejection of divalent ions	>99%	
		rejection of organics	50-90, depends on pre-treatment and some organics are volatile	*Water desalting, planning guide for water utilities, AWWA*
		rejections of colloids	100%	
		biological stability	fine	
		water quality	pure water with TDS concentration of 2-10mg/l	*Technical assessment of produced water treatment technologies, 2009*
	Waste streams	***discharge problems***	no, because of low recovery rates	
		water quality	not very concentrated due to low recovery rates, limited chemical	
		valuables recovery possible	heat , part of the brine can be recirculated into the incoming feed water	
Process parameters	Water recovery	10-30% for salt water desalination		*Technical assessment of produced water treatment technologies, 2009*
	Capactity limits	plants generally only cost effective with very large capacity >1,000m^3/d		
	Flexibility in operation	MSF can easily be adapted to high variety in water quality but not in water quantity. System is not tuneable		*Technical assessment of produced water treatment technologies, 2009*
	Fouling control	scale inhibitors can be used to reduce scaling in heat transfer surfaces		*Technical assessment of produced water treatment technologies, 2009*
	Cleaning of the system	cleaning with an acid and mechanical cleaning are periodically needed		
	Space requirements	a MSF plant generally requires a lot of space		
	Life span of the system	typically 20 years		*Technical assessment of produced water treatment technologies, 2009*
	Thermal energy demand	250-330 kJ/kg		*Sustainable water for the future, water recycling versus desalination, 2010*
Costs	Capital costs	0,42-1,40 euro ct/m^3 for SW desalination, capacity: 23,000-528,000 m^3/d (not indicated what costs include)		*water desalination cost literature: review and assessment, Ioannis (2007)*
	Operational costs	***energy requirement***	3-5 kWh/m^3	*Sustainable water for the future, water recycling versus desalination, 2010*
		chemical requirement	0,04 euro/m^3	*Sustainable water for the future, water recycling versus desalination, 2010*
Further information	Main suppliers			
	Reference projects	numerous, mainly in the middle east		
	Research needs			
	Recommended literature	a lot of literature available on MSF research, see also references		

Category	Name	Sub criteria/ Notes	Reference
Technology	Name	**Multi Effect Distillation (MED)**	
	Description	MED is a thin-film evaporation approach, where the vapor produced by one chamber (="effect") is subsequently condensed in the next chamber. This chamber has a lower temperature and pressure, providing additional heat for vaporization. Driving force: heat	
	Status	full scale	
	Most common applications	desalination of brackish and sea water, especially in warm areas like the middle east. Often combined with power generation	
Water quality	Influent quality requirement	***pre-treatment needed*** yes, but only to remove large particles ***type of pre-treatment*** sand filtration, coagulation, sedimentation ***limiting factors*** availability of heat ***salinity range TDS*** 8,000-50,000 mg/L ***fouling extent*** major problem is scaling in heat transfer surfaces	*Water desalting, planning guide for water utilities, AWWA*
	Effluent quality possibilities	***rejection of monovalent ions*** >99% ***rejection of divalent ions*** >99% ***rejection of organics*** 50-90, depends on pre-treatment and some organics are volatile ***rejections of colloids*** 100% ***biological stability*** fine ***water quality*** pure water with TDS concentration of 2-10mg/l	*Water desalting, planning guide for water utilities, AWWA* *Technical assessment of produced water treatment technologies, 2009*
	Waste streams	***discharge problems*** no, because of low recovery rates ***water quality*** not very concentrated due to low recovery rates, no chemicals ***valuables recovery possible*** heat , part of the brine can be recirculated into the incoming feedwater	
Process parameters	Water recovery	can be up to 65% for seawater desalination with vertical tube design	*Water desalting, planning guide for water utilities, AWWA* *Technical assessment of produced water treatment technologies, 2009*
	Capactity limits	plants generally only cost effective with very large capacity >1,000m^3/d	*Water desalting, planning guide for water utilities, AWWA*
	Flexibility in operation	MED can easily be adapted to high variety in water quality but not in water quantity. System is not tuneable	*Technical assessment of produced water treatment technologies, 2009*
	Fouling control	scale inhibitors can be used to reduce scaling in heat transfer surfaces	*Technical assessment of produced water treatment technologies, 2009*
	Cleaning of the system	cleaning with an acid and mechanical cleaning are periodically needed	
	Space requirements	depends on feed water and required effluent quality. Indication for plant with capacity of 37,850m^3/day = 6000m^2 (seawater desalination)	*Water desalting, planning guide for water utilities, AWWA*
	Life span of the system	Typically 20 years	*Technical assessment of produced water treatment technologies, 2009*
	Thermal energy demand	145-390 kJ/kg	*Sustainable water for the future, water recycling versus desalination, 2010*
Costs	Capital costs	for SW desalination with a plant capacity <100 m^3/d, costs: 2-8 euro/m^3 (not indicated what is included in the costs)	
	Operational costs	***energy requirement*** 1,5-2,5 kWh/m^3 ***chemical requirement*** 0,06 euro/m^3	*Sustainable water for the future, water recycling versus desalination, 2010* *Sustainable water for the future, water recycling versus desalination, 2010*
Further information	Main suppliers		
	Reference projects	numerous, mainly in the middle east	
	Research needs		
	Recommended literature	a lot of literature available on MED research, see also references	

Category	Name	Sub criteria/ Notes		Reference
Technology	**Name**	**Electrodionization (EDI)**		
	Description	anion and cation exchange membranes are arranged in alternating series which form and individual cell between 2 electrodes. the feed cell is filled with a mixed bed ion exchange resin which adsorbs the ions from the feed stream and enhances migration into the concentrate cell. water in the feed cell is depleted with ions and produces the dilute. driving force: 2 step: 1) concentration gradient, 2) electrical potential		*Ion exchange membrane sepatration procesess, Strathmann*
	Status	full scale		
	Most common applications	production of ultra pure water for the industry, generally a polishing step after RO		
Water quality	**Influent quality requirement**	***pre-treatment needed***	yes, mainly removal of particles and organic matter	
		type of pre-treatment	RO is the most applied, UF is also possible depending on the feed water quality	
		limiting factors	transport capacity of the resins	
		salinity range	max conductivity 50 µS/cm, but there are examples of higher influent TDS	*Production of ultrapure water by continuous deionization, Wood et al (2009)/ high-purity water preparation, Meltzer*
		fouling extent	limited when pre-treatment is sufficient	
	Effluent quality possibilities	***rejection of monovalent ions***	100%	
		rejection of divalent ions	100%	
		rejection of organics		
		rejections of colloids	100%	
		biological stability	stable, no biological components present	
		water quality	ultra-pure water <10 TDS mg/l	
	Waste streams	***discharge problems***	no	
		water quality	5 to 10 times more concentrated then feed water (no chemicals)	*Production of ultrapure water by continuous deionization, Wood et al. (2009)*
		valuables recovery possible	concentrate can be reclaimed for other uses	*Production of ultrapure water by continuous deionization, Wood et al. (2009)*
Process parameters	**Water recovery**	80-90% for water polishing		
	Capacity limits	generally limited by costs		
	Flexibility in operation			
	Fouling control	not needed/applied		
	Cleaning of the system	not needed/applied		
	Space requirements	similar to an ED plant; depends on feed water and required effluent quality.		
	Life span of the system	up to 5 years		*The Nalco waterhandbook*
Costs	**Capital costs**	No good indication available, but comparable with ED costs but resin costs should be taken into account		
	Operational costs	***energy requirement***	0,25kWh/m^3	*Production of ultrapure water by continuous deionization, Wood et al. (2009)*
		chemical requirement	no chemicals, because regeneration of resins is not needed	
Further information	**Main suppliers**			
	Reference projects			
	Research needs			
	Recommended literature			

Category	Name	Sub criteria/ Notes		Reference
Technology	**Name**	**Ion Exchange (IEX)**		
	Description	removal of specific ions or compounds from water by the exchange of a pre-saturated ion via an IX resin in a filter bed. Cation resins are available to remove cationic solutes and anion resins to remove anionic solutes. Mixed bed always required for desalination purpose with IEX		
	Status	full scale		
	Most common applications	drinking water, industry water --> softening, polishing, removal of organic compounds		
Water quality	**Influent quality requirement**	***pre-treatment needed***	yes, predominantly removal of suspended solids	
		type of pre-treatment	sand filtration, UF, coagulation, sedimentation	
		limiting factors	exchange capacity of the resins	
		salinity range TDS	500-7.000 mg/l	
		fouling extent		
	Effluent quality possibilities	***rejection of monovalent ions***	can be up to 99% but depends on type of resin (weak/strong and affinity of ions)	
		rejection of divalent ions	can be up to 99% but depends on type of resin (weak/strong and affinity of ions)	
		rejection of organics	depends on nature of the organics	
		rejections of colloids		
		biological stability	IEX is not a barrier for microorganisms	
		water quality	depends on type of resin <1,0 mg TDS/l	
	Waste streams	***discharge problems***	treatment required	
		water quality	the brine is a very concentrated waste stream	
		valuables recovery possible	none	
Process parameters	**Water recovery**	depends on regeneration needs, can be up to 98%		*Water desalting, planning guide for water utilities, AWWA*
	Capacity limits	can be cost effective for all ranges of plant capacity		
	Flexibility in operation	Pre-treatment is of great influence of performance of the system, but system is more robust than membrane processes. Process is not tuneable.		
	Fouling control	resin bed can be periodically backwashed, addition disinfection can be done to limit biological activity in the bed		
	Cleaning of the system	regeneration of the resins, in case of SW of BW very often needed		
	Space requirements	depends on water quality and volume, extra space required for chemical storage		
	Life span of the system	resins bed needs to be replaced after a certain period, depends on feed water quality		
Costs	**Capital costs**	no good indication found for desalination example		
	Operational costs	***energy requirement***	only for operating the process	
		chemical requirement	very high for BW and SW due to regeneration costs	
Further information	**Main suppliers**			
	Reference projects	numerous		
	Research needs			
	Recommended literature	a lot of literature available on IEX research, see also references		

Category	Name	Sub criteria/ Notes		Reference
Technology	**Name**	**Capacitive Deionization (CDI)**		
	Description	With CDI ions are removed from water by adsorption onto the surface of porous electrodes by applying a low voltage electric field. This is called membrane capacitive deionization and is a modification of the classical CDI. CDI makes use of aerogels in stead of membranes. (factsheet focusses on membrane		
	Status	demo		
	Most common applications	desalination of brackish water		
Water quality	**Influent quality requirement**	***pre-treatment needed***	removal of TOC and scaling factors	*CDI for desalination and water treatment - past present and future (a review), Oren (2007)*
		type of pre-treatment	sand filtration, UF, coagulation, sedimentation	
		limiting factors	organic content	*Sustainable water for the future, water recycling versus desalination, 2010*
		salinity range TDS	<3.000 mg/L, can be up to 8.000 but not common	*Technical assessment of produced water treatment technologies, 2009/ water desalting, planning guide for water utilities, AWWA*
		fouling extent	research need	
	Effluent quality possibilities	***rejection of monovalent ions***	seems to have preference over divalent ions	*Sustainable water for the future, water recycling versus desalination, 2010*
		rejection of divalent ions	seems to be removed less then monovalent ions	*Sustainable water for the future, water recycling versus desalination, 2010*
		rejection of organics	no, organics generally pass through the CDI process	
		rejections of colloids	>90%	
		biological stability	CDI is not a barrier for microorganisms	
		water quality		
	Waste streams	***discharge problems***	treatment needed due to high concentrations	
		water quality	very concentrated as it is only flush water (no chemicals)	
		valuables recovery possible	salt can be recovered	
Process parameters	**Water recovery**	up to 80-90% for salt water desalination		*Voltea*
	Capacity limits	Voltea does not have a standard industrial system larger than 13m^3/h yet (small size)		
	Flexibility in operation	high level of robustness, flexibility and reliability, process is tuneable		*Technical assessment of produced water treatment technologies, 2009/ water desalting, planning guide for water utilities, AWWA*
	Fouling control	research need		
	Cleaning of the system	regeneration by reversing the electrode polarity		*Voltea*
	Space requirements	a compact and mobile installation		*Voltea*
	Life span of the system	expected to be 10 years		
Costs	**Capital costs**	no good indication available		
	Operational costs	***energy requirement***	0,2-0,6 kWh/m^3	*Voltea*
		chemical requirement	no chemicals required	*Technical assessment of produced water treatment technologies, 2009/ water desalting, planning guide for water utilities, AWWA*
Further information	**Main suppliers**	Voltea (Netherlands)		
	Reference projects			
	Research needs	main research needs are fouling and scaling of the system , effects of humics on electrodes		*CDI for desalination and water treatment - past present and future (a review), Oren (2007)*
	Recommended literature			

Appendix B.

In this appendix the graphs for the determination of the LCD for different salts, salt concentrations and at various flow rates are presented. The minimum of the graph indicates the LCD, and the value of the LCD is given above the graph. The LCD determined from the graph with the different NaCl concentrations together result in the linear relation given in Figure 4-2. The four different LCD graphs for varying flow rate result in the linear relation given in Figure 4-3. The last graph in this appendix shows the LCD for different salt concentrations in model waters.

40mmol/l NaCl - LCD = 171.8A/m^2

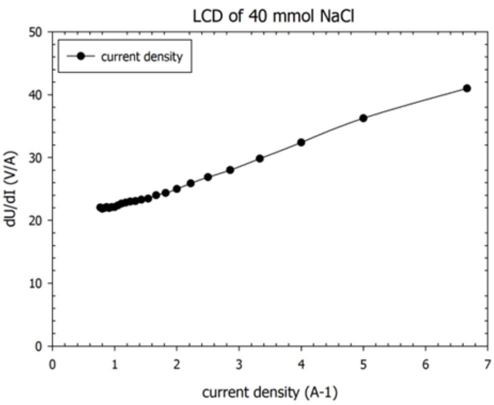


Figure 9-1 Limiting current density of 40mmol/l NaCl

30mmol/l NaCl - LCD = 140.6A/m^2

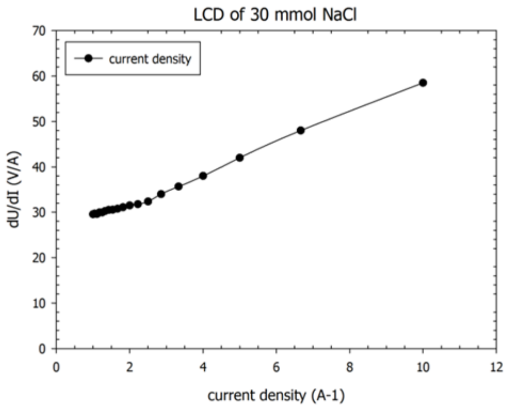


Figure 9-2 Limiting current density of 30mmol/l NaCl

25mmol/lNaCl - LCD = 117.2A/m^2

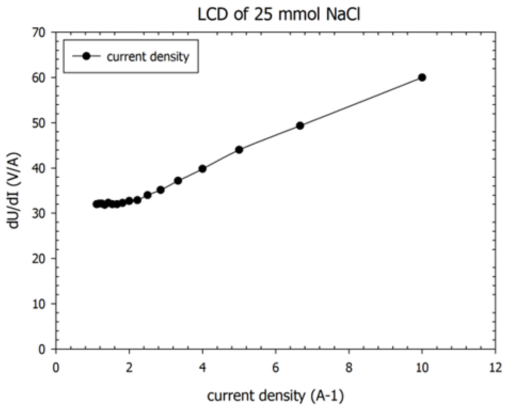


Figure 9-3 Limiting current density of 25mmol/l NaCl

20mmol/l NaCl - LCD = 96.9A/m^2

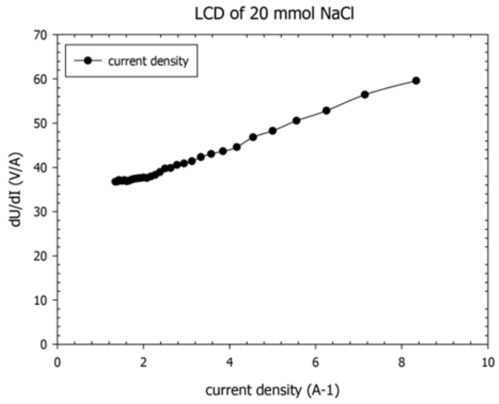


Figure 9-4 Limiting current density of 20mmol/l NaCl

10mmol/l NaCl - LCD = 56.3A/m^2

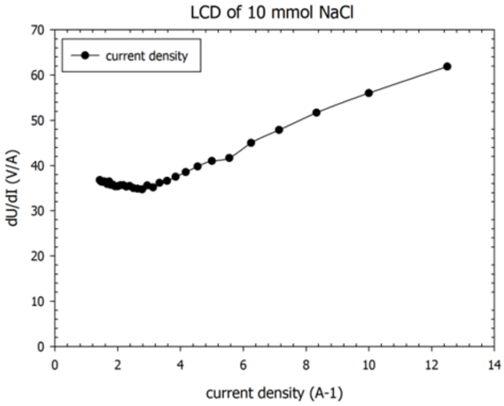


Figure 9-5 Limiting current density of 10mmol/l NaCl

5mmol/l NaCl - LCD = 34.4A/m^2

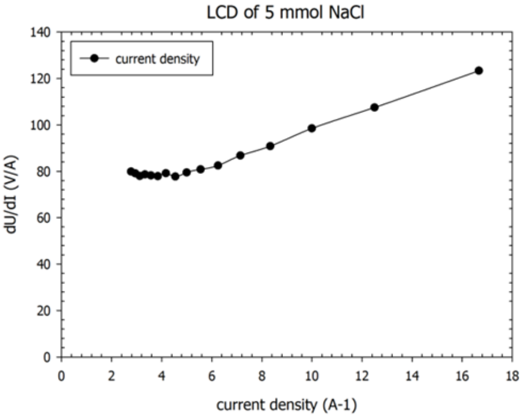


Figure 9-6 Limiting current density of 5mmol/l NaCl

3.4mmol/l NaCl - LCD = 34.3A/m^2

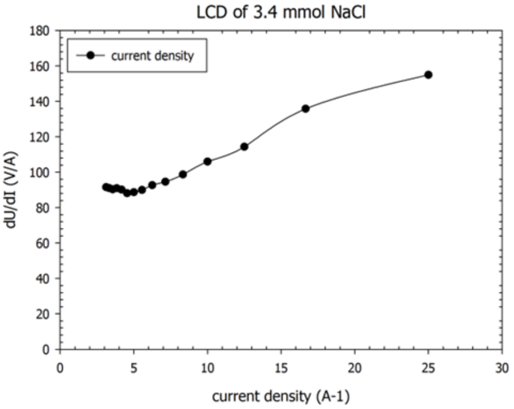


Figure 9-7 Limiting current density of 3.4mmol/l NaCl

1.7mmol/l NaCl - LCD = 25.0A/m^2

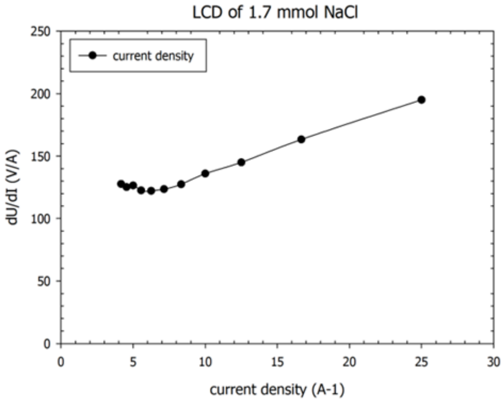


Figure 9-8 Limiting current density of 1.7mmol/l NaCl

10mmol/l v-9cm/s - LCD = 40.6A/m^2

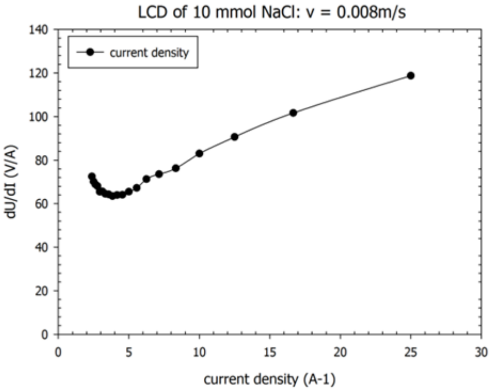


Figure 9-9 Limiting current density of 10mmol/l NaCl v=8cm/s

10mmol/l v = 17.6m/s - LCD = 62.5A/m^2

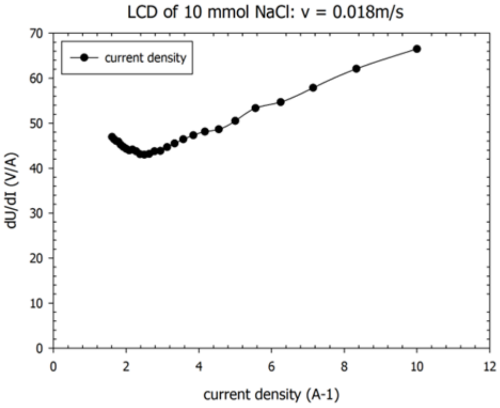


Figure 9-10 Limiting current density of 10mmol/l NaCl v=17.6cm/s

10mmol/l v = 17.6m/s - LCD = 68.8A/m^2

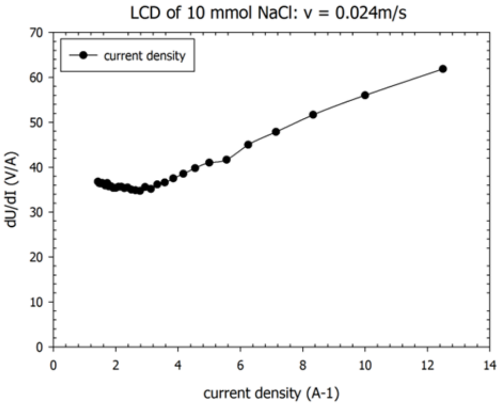


Figure 9-11 Limiting current density of 10mmol/l NaCl v=23.8cm/s

10mmol/l v = 17.6m/s - LCD = 78.1A/m^2

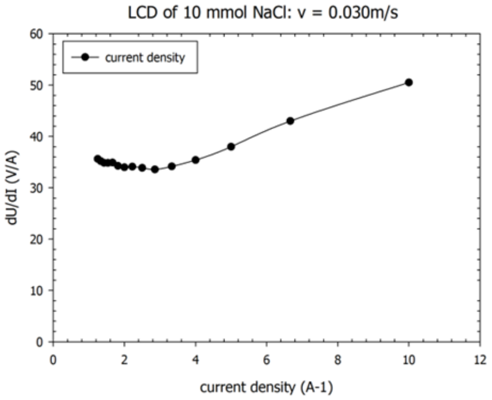


Figure 9-12 Limiting current density of 10mmol/l NaCl v=29.8cm/s

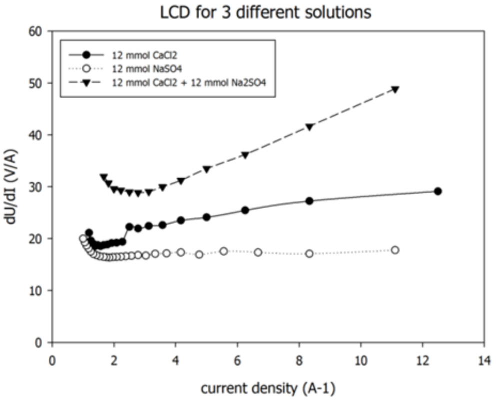


Figure 9-13 Limiting current density of different salt solutions

Appendix C.

The membranes in the ED stack were cleaned after each series of experiments, to restore the capacity and low resistance of the membranes. A constant current (0.5A) experiment with 10mmol/l NaCl for diluate and concentrate was carried out to determine the desalination rate and the voltage profile of the fouled membranes. After this experiment, the ED stack was opened up, and the membranes were removed from the stack and stored in a 3M NaCl solution overnight. Figure 9-14 shows the soaking of the membranes and Figure 9-15 the disassembled ED stack. After soaking them in this solution, a brown colour came of the membranes. The electrodes, spacers and membranes were rinsed with tap water before they were put back in the stack. The stack was connected again and screws were tightened by hand, where after the system was checked for leakages. With the system put back together again, a constant current (0.5A) experiment of 10mmol/l NaCl for diluate and concentrate was carried out to determine the desalination rate and the voltage profile of the cleaned membranes. In Figure 9-16 the voltage profile of 2 cleaning experiments are presented: cleaning after LCD experiment with different water types and cleaning after the 10 CTBD water runs. The figure shows the voltage profile of the cleaned membranes is, in both situations, close to the reference profile. It can also be observed from the graph that after the limiting current density the membranes were more fouled compared to the 10 CTBD water runs.

Figure 9-14 Soaking of the ED membranes in NaCl solution

Figure 9-15 Disassembled ED stack

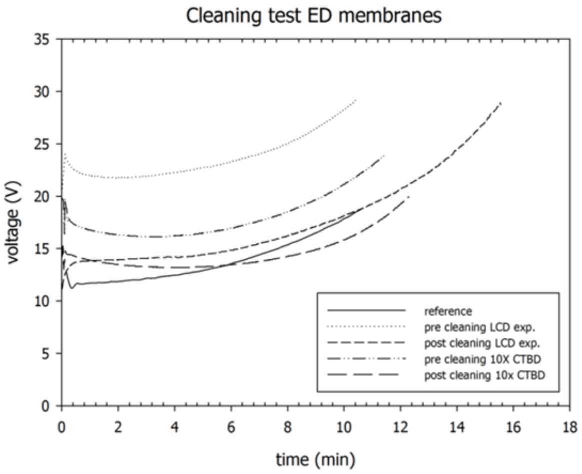


Figure 9-16 Cleaning test - voltage profile

Appendix D.

The calculations of the dimensions of the ED pilot are presented in this appendix.

General

The calculations are based on the assumption that sodium chloride fully contributes to the salt concentration in the feed water, and thus only NaCl is removed. In practice, cooling tower blowdown water also contains high concentrations of calcium and sulphate. The other starting points are:

$1 ion = 1\ electron$
$Q\ per\ diluate\ or\ concentrate\ compartment = 1.0\ l/min$, this value is chosen based on the required flow rate in the stacks.
$Constant\ of\ Avogadro = 6.02214 * 10^{23}$
$1\ electron = 1.6022 * 10^{-19}\ Coulomb$

The calculation of the desalination in the stacks is elaborated for the first stack. The calculations for the other 3 stacks are given in Table 9-1.

Desalination in EDR stack 1

Required removal of conductivity is 1200µS/cm, which is equivalent to $9.6\, mmol/l\ \ NaCl$ (based on calibration curve given in Figure 9-17)

Salt removal: $\frac{9.6*1}{60} = 0.16\, mmol/s$

Current needed: $0.16 * 6.02214 * 10^{23} * 1.6011 * 10^{-19} = 15437.9\, mA = 15.44A$

With a membrane area of a commercial stack being $0.5 * 0.5m^2$

The current density = $\frac{15.44}{0.5*0.5} = 61.75\ \ A/m^2$

The limiting current density of the water in this stack is $107.05\, A/m^2$, (based on relation given in Figure 9-18). So below the applied current density is below the limiting current density, which is preferred for a good operation of the system.

Table 9-1 EDR stack properties for desalination

	Stack 1	**Stack 2**	**Stack 3**	**Stack 4**
Conductivity water entering stack (µS/cm)	4000	2800	1900	1300
Conductivity water leaving the stack (µS/cm)	2800	1900	1300	1000
Salt removal (µS/cm)	1200	900	600	300
NaCl eq. (mmol/l	9.6	6.6	3.6	0.6
Salt removal (mmol/s)	0.16	0.11	0.06	0.01
Current needed (A)	15.4	10.6	5.8	1.0
Current density (A/m^2)	61.8	42.5	23.2	3.9
LCD of water leaving the stack (A/m^2)	107.0	69.7	44.8	32.3

Number of cell pairs per stack

With a chosen value of $1.0\ l/h$ per cell = $Q\ in\ diluate\ or\ concentrate\ compartment = 1.0 * 10^{-3} * 60 = 0.06\ m^3/h$

The number of cell pairs for the treatment of $4.0\ m^3/h$ is:

$$No.of\ cell\ pairs = \frac{4}{0.06} = 66.66\ pairs$$

The number of cell pairs in a stack is 67. The velocity of the water in the stack is:

$$v_{stack} = \frac{\frac{0.06}{0.5 * 7 * 10^{-4}}}{3600} = 0.048 m/s$$

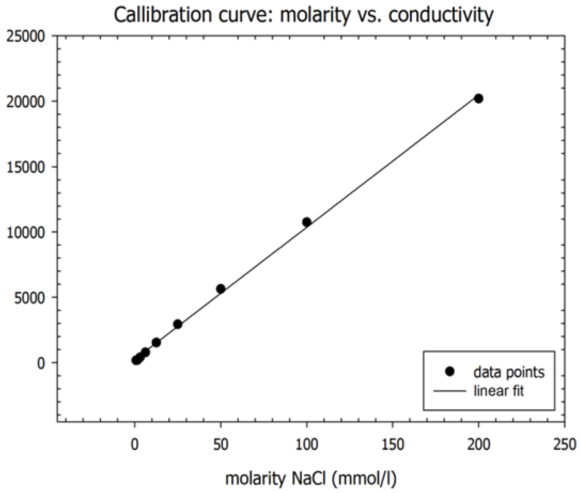


Figure 9-17 Calibration curve sodium chloride solutions

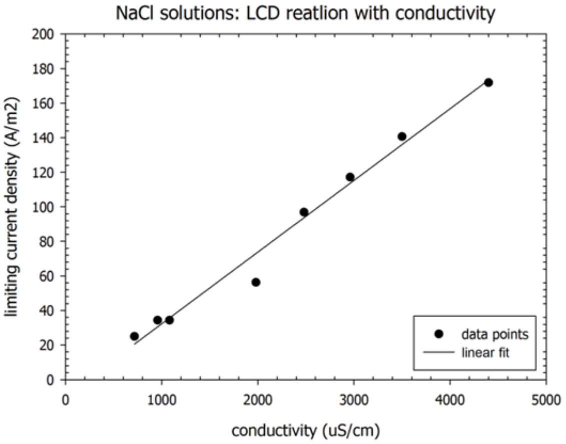
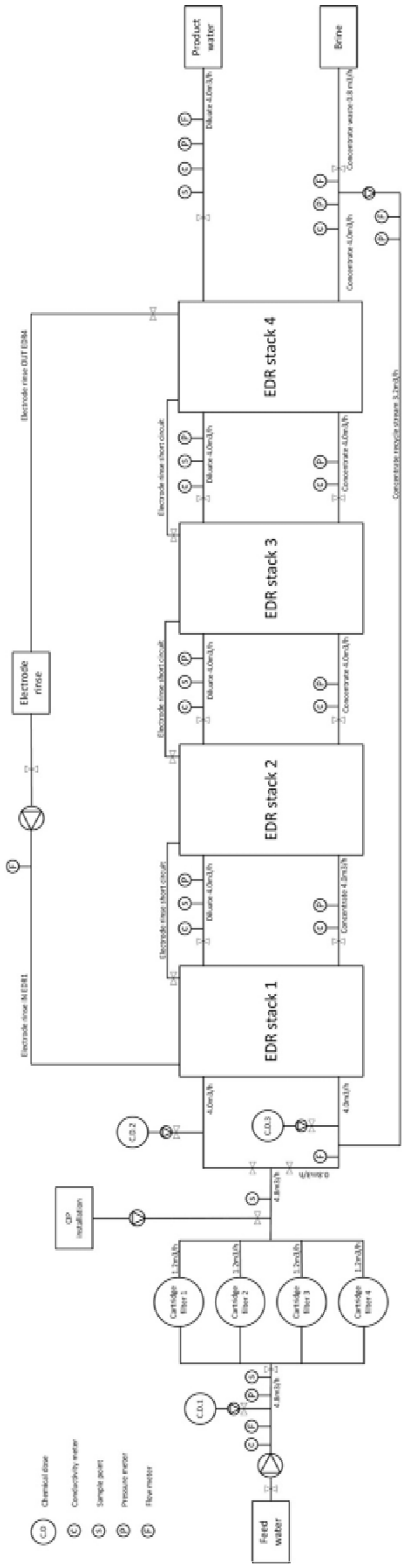


Figure 9-18 Limiting current density as a function of the conductivity for NaCl solutions

Process and flow diagram electrodialysis reversal pilot design.



Appendix E.

To investigate the influence of staging the current on the salt removal and the voltage profile in electrodialysis, an experiment was carried out. A volume of 2L 25mmol/l NaCl (ca. 3000µS/cm) was taken as a feed for the diluate stream. The concentrate was prepared as 1L 0.1mol/l NaCl solution. Flows and other parameters during the experiment were similar to the approach which is explained in the materials and methods section. At the start of the experiment a constant current of 0.4A was applied over the ED stack. Once the conductivity of the diluate dropped below 2250µS/cm, the constant current was lowered to 0.2A. In the third stage the constant current was lower to 0.1A, once a conductivity of 1500µS/cm was achieved. The currents and the moment of shifting were determined based on the conductivity of the water and the current densities in the 3 stages. Figure 9-19 shows that the conductivity of the diluate drops faster when a larger constant current is applied on the ED stack. The energy demand for a staged current operation is calculated from the voltage profile given in

Figure 9-20 by multiplying the constant current with the average voltage over the three stages. The voltage graph of the 3 stages was extrapolated to determine the energy demand of an experiment with just one constant current (0.4A, 0.2A or 0.1A), as shown in Figure 6-3 in Chapter 6.

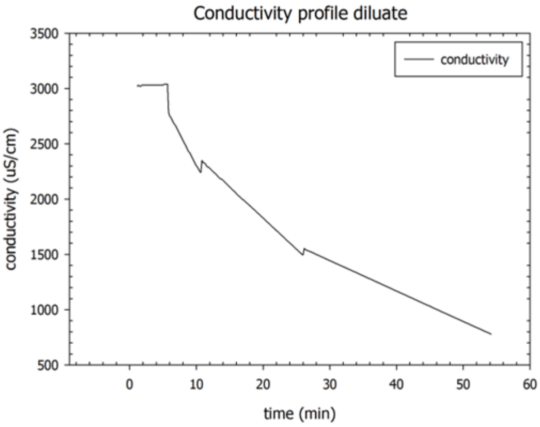


Figure 9-19 Conductivity profile, staged CC experiment

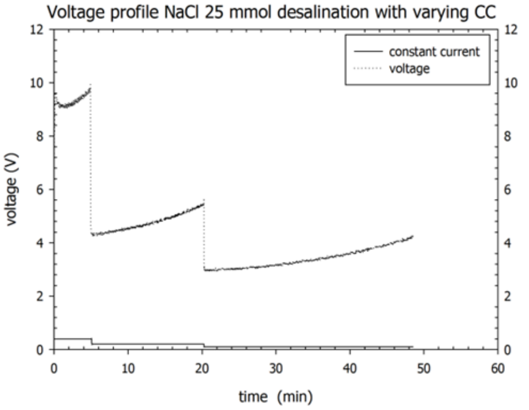


Figure 9-20 Voltage profile, staged CC experiment

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